PROJECT COMPLETION REPORT

FACTORS CONTROLLING VARIATIONS IN RIVER WATER QUALITY IN KANSAS

by

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ABSTRACT

FACTORS CONTROLLING VARIATIONS IN RIVER WATER QUALITY IN KANSAS

The most important factor controlling the quality of river waters in Kansas is the variation in the amounts and chemistry of quickflow (reflecting dissolution of constituents from soils and near surface alluvium) versus baseflow (mainly groundwater inflow). Given similar bedrock, the higher the average annual precipitation and the lower the average evaporation rate, the lower the total dissolved solids (TDS) of both quickflows and baseflows. Quickflows have lower TDS and Na/(Na + Ca) than baseflows. Primary sources of high TDS in baseflows are saline formation waters and dissolution of halite and gypsum; in western and central Kansas evaporative concentration also contributes to high TDS and can increase Na/(Na + Ca) slightly by calcite crystallization. Two types of cyclic relationships occur in chemical hydrographs of precipitation or snowmelt events: a quickflow flushing-dilution cycle follows a counterclockwise loop and a quickflow dilution-saline groundwater discharge cycle a clockwise loop when discharge is plotted versus specific conductance, TDS, or Na/(Na + Ca). A procedure is proposed for controlling the quality of river waters receiving saline groundwaters: a system of small flood retarding and recharge structures with baseflow release drains should be built far enough upstream of saline inflow areas, that groundwater recharge increases good quality baseflow and decreases mineralized discharges.

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INTRODUCTION

The quality of river waters varies widely in Kansas, not only from one location to another, but with time at individual sites. River waters in much of western and central Kansas are high in dissolved solids during most of the year and thus are less than desirable for irrigation or drinking. In many areas appreciable amounts of halite and gypsum present in the bedrock dissolve producing mineralized waters that enter the river in groundwater inflow. Saline formation waters also affect the quality of groundwater discharge into some rivers. Evapotranspiration of irrigation waters and soil moisture increases the concentrations of salts in soil solutions or on soil particles. The more soluble salts are then removed by overland flow and interflow to the rivers. Evaporation from reservoir and river surfaces further increases the dissolved solids by concentrating the waters.

Most of the variation in river water quality with time is related to changes in discharge. In general, high discharges are much lower in dissolved minerals than low flows. However, plots of discharge versus total dissolved solids show wide scatter for rivers in Kansas indicating additional factors important in controlling river quality. Not only the amounts of dissolved constituents vary but also the relative concentrations of the constituents change with flow.

Present models of variations in dissolved inorganic constituents in Kansas rivers are as yet not able to predict with sufficient certainty the water chemistry of many rivers. Good predictions would be useful in water management such as determining optimum use times, allowing preparation time for expected periods of lower quality water, or designing precedures by which the river quality could be improved.

A knowledge of the existing controls on river water quality is necessary for improved identification and quantification of point and non-point sources of pollution. The natural factors controlling variations in the particular constituents of interest must be determined and separated in order that the anthropogenic sources can be seen. Understanding of the factors is also needed to establish baseline variations in river water chemistry, against which future changes could be compared and evaluated.

Therefore, objectives of this study were the following: 1) to determine the principal factors controlling variations in the concentration of major dissolved constituents in river waters and the relative importances of each factor in different geological and climatic regions of Kansas. Emphasis was placed on those rivers with generally high dissolved solids and widely varying chemistry which are located in central and western Kansas. Controls on the variations in quality considered were quickflow chemistry (including the effects of direct precipitation, overland flow, and rapid interflow), baseflow chemistry (involving the effects of delayed interflow and groundwater flow), and the evaporation-crystallization process by which dissolved constituents are concentrated by evaporation and $CaCO_3$ crystallizes. 2) To describe variations in river water chemistry associated with changes in single event (storm or snowmelt), seasonal, and yearly discharges based on the contribution of each of the above controlling factors for each river. 3) To determine the type and period of high discharge events in which the water quality of rivers normally high in dissolved solids would meet standards for irrigation and drinking water use. 4) To improve the identification of point and non-point sources of stream water pollution by establishing the relative contributions of the different natural factors controlling inputs of major constituents.

The principles determined in the research should be generally applicable to the Great Plains and any other comparable regions. Similar investigations could be made for other areas based on the use of the procedures developed.

DESCRIPTION OF STUDY AREAS

General Site Selection

Representative river sites were selected from water quality stations of the U. S. Geological Survey in both the two major drainage basins of Kansas, the Kansas River and Arkansas River systems. Each station selected had several years or more of published chemical analyses of samples collected at least once a month. Specific sites used in the study and general characteristics of the rivers at these points are given in Table 1. Locations of the river stations are shown on a map of Kansas in Figure 1.

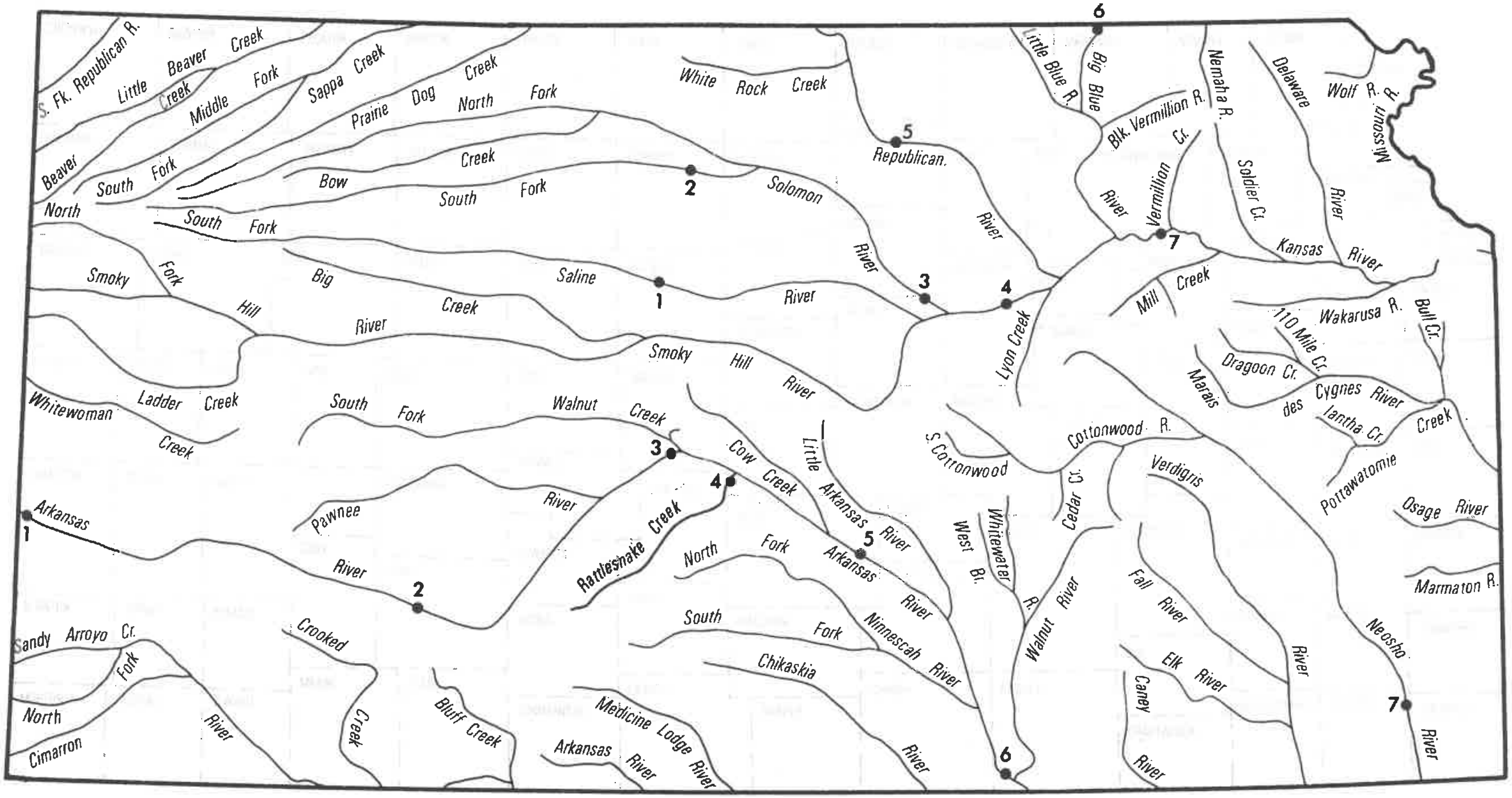
In the Kansas River basin a site was selected for each main tributary to the main river, and also a station on the Kansas River which represents the combined effects of the tributaries on water quality. Specific locations on the tributaries were chosen to facilitate comparison of the effects on river chemistry of different climatic and geologic regions within the basin. Important climatic factors are precipitation and potential evaporation. Geologic influences can be separated into the main categories of calcareous rocks with and without appreciable amounts of gypsum, strata containing saline formation water which seeps into streams and rivers, and a halite deposit where it is near the surface and dissolving to produce brines discharging into rivers. Tributary stations investigated were also those which were least affected by reservoir discharges, either located above any reservoirs, or situated far downstream of reservoirs.

Most of the stations selected in the Arkansas River basin were on the Arkansas River and spaced such that effects of changes in climate and geology were large. The only tributary entering the Arkansas River within Kansas which was studied, Rattlesnake Creek, represented the strong influence of saline water input from dissolution of subsurface

Table 1. River Water Quality Stations Used in This Study

River	Station Location	U.S.G.S. Station Number	Location Number in Figure 1	Drainage Area (mi^2)	Average Discharge (cfs)	Water Year Data Used in this Study
			Kansas River Basin			
Saline	Russell	8670	1	1,502	112	1965-75
S. Fork Solomon	Osborne	8740	2	2,012	127	1965-77
Solomon	Niles	8759	3	6,770	563	1965-77
Smoky Hill	Enterprise	8776	4	19,260	1613	1965-77
Republican	Concordia	8560	5	23,560	748	1965-77[a]
Big Blue	Oketo	8824	6	4,444	765	1964-73
Kansas	Wamego	8875	7	55,280	4858	1965-75
			Arkansas River Basin			
Arkansas	Coolidge	1375	1	25,410	194	1964-68, 1970-73, 1975-77
Arkansas	Dodge City	1395	2	30,600	195	1964-77
Arkansas	Great Bend	1413	3	34,356	355	1964-75
Rattlesnake	Raymond	14262	4	1,167	61	1964-70
Arkansas	Hutchinson	14333	5	38,910	646	1964-77
Arkansas	Arkansas City	1465	6	43,713	1819	1964-68, 1974-77
Neosho	Parsons	1835	7	4,905	2558	1965-75

[a] Data for 1975-77 was from the station at Clay Center.



Kansas River Basin
1. Saline River near Russell
2. South Fork Solomon at Osborne
3. Solomon River at Niles
4. Smoky Hill River at Enterprise
5. Republican River at Concordia
6. Big Blue River near Oketo
7. Kansas River at Wamego

Arkansas River Basin
1. Arkansas River near Coolidge
2. Arkansas River at Dodge City
3. Arkansas River at Great Bend
4. Rattlesnake Creek near Raymond
5. Arkansas River near Hutchinson
6. Arkansas River at Arkansas City
7. Neosho River near Parsons

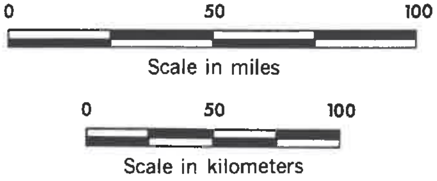


Figure 1. Location of River Stations Studied.

halite. The Neosho River site was chosen as indicative of the chemistry of rivers in southeastern Kansas, the area of the state with the greatest rainfall, lowest evaporation rates, and least effect of highly mineralized groundwater on river chemistry. This provided a contrast of waters low in dissolved solids with all the other river stations investigated in the basin which have high dissolved solids concentrations.

Kansas River Basin Stations

Saline River near Russell. The head of the watershed of the Saline River is underlain by the silts, sands, and gravels of the Ogallala Formation, which in turn is generally covered by a montle of loess. Flow is received from this area during large rainstorms or amounts of snowmelt. A large part of the bedrock over which the Saline River flows upstream of Russell is composed of Cretaceous limestone, chalk, shale, and sandstone. The strongest influence on the chemistry of water in the river is the seepage of saline water from sandstone of the Dakota Formation. For example, chloride concentrations of baseflow from Salt Creek, a tributary joining the Saline River two miles upstream from the water-quality station, are several thousand mg/l. No reservoirs are upstream of the station.

South Fork Solomon River at Osborne. The drainage basin of the South Fork of the Solomon River overlies geology similar to that as the Saline River basin, except that at Osborne the river has not eroded to the Dakota Formation. Thus, this water-quality station provides a comparison of drainage largely from Cretaceous sediments without the influence of saline formation water, with the Saline River basin where the saline seepage is the principal control on baseflow chemistry. The Webster Reservoir is 65 miles upstream of the Osborne station. Almost half of the watershed area at Osborne, however, is below the reservoir, and the basin of the reservoir is in a drier climate than that between the reservoir and Osborne. Thus, most of the flow received at Osborne is unaffected by the reservoir.

Solomon River at Niles. The flow of the Solomon River at Niles is also somewhat affected by a reservoir. Waconda Lake is not the major control on the flow at Niles, for the dam is 151 miles upstream and has an average discharge only 25 percent that at Niles. The chemistry of the Solomon River at this water-quality station mainly reflects flow over Cretaceous bedrock and soils derived therefrom, and includes the effect of saline seeps from the Dakota Formation and Cheyenne Sandstone, although these are diluted more than in the Saline River.

Smoky Hill River at Enterprise. The Smoky Hill River at the Enterprise station drains all of the area included in the previous sites, but has an additional major influence on its water chemistry not found in the upstream sites, that is, the inflow of brines derived from the solution of halite beds in the Permian Wellington Formation. The halite, as well as gypsum and anhydrite, is located in near surface Permian rocks. Together these minerals supply large additions of Na, Ca, Cl, and SO_4 to the river by way of flow through the alluvium between New Cambria and Solomon.

Republican River at Concordia. The watershed of the Republican River at Concordia is underlain largely by the Ogallala Formation mantled with loess, and in a small part in the eastern part by Cretaceous carbonates and shales. At Concordia there is no influence of saline seepage from the Dakota Formation. A couple years of data was also used from the Clay Center stations because the Concordia station was discontinued. Although the Republican River has cut through the Dakota Formation at Clay Center, the effect of saline seepage is very minor, because most of the formation waters in the sandstone in this area have been flushed out or diluted by infiltrating meteoric water. The drainage basin of the Republican River at Concordia represents control on water quality from similar geology as in the basin of the South Fork of the Solomon River at Osborne. However, the area is farther to the north where potential evaporation rates are lower, and includes area farther to the east with higher average precipitation, resulting in more dilute flow. Reservoirs do not affect the flow at the Concordia station.

Big Big Blue River near Oketo. The Big Blue River drains an area of Cretaceous limestone, shale, and sandstone, and Permian limestone and shale. In the headwaters of the basin much of the bedrock is overlain by alluvial sediments or loess, and in the area just north of the Kansas-Nebraska border, some of the bedrock is covered by glacial till. The water-quality station at Oketo was chosen for the Big Blue River because it is upstream of Tuttle Creek Reservoir and thus is free of flow regulation unlike the Manhattan site. Being even farther to the north and east of the previous sites, smaller evaporation and greater annual precipitation mean that saline formation waters from Cretaceous rocks, and dissolution of gypsum from Permian strata are diluted more.

Kansas River at Wamego. The total of all factors affecting water quality in the tributaries to the Kansas River past its junction with the Big Blue River are summed in the station at Wamego. Little additional drainage is received between the junction and Wamego. Two dams downstream of tributary stations considered in this report appreciably control the flow of the river at Wamego, namely Tuttle Creek and Milford reservoirs.

Arkansas River Basin Stations

Arkansas River near Coolidge. Waters in the Arkansas River from the Rocky Mountains is low in dissolved solids, but steadily decreases in flow and increases in dissolved loads as it flows across very dry, high plains of southeastern Colorado. In the plains the river crosses areas underlain by Mesozoic limestone, shale, and sandstone which contain some gypsum. Dissolution of the gypsum and flow of the solutions in tributaries to the Arkansas River, followed by concentration by evaporation from the river surface, the John Martin Reservoir, and irrigation waters, result in very high Ca and SO_4 concentrations in the river by the time it reaches Coolidge.

Arkansas River at Dodge City. The main expected controls on the chemistry of the Arkansas River between Coolidge and Dodge City are opposite in effect, being concentration by evaporation and dilution by additional flow through loess, the Ogallala Formation, and dune sands which contain no saline formation waters or very soluble minerals.

Arkansas River at Great Bend. In addition to the type of sediments underlying the Arkansas River basin between Coolidge and Dodge City, a small amount of drainage is received from Cretaceous shale, limestone, and sandstone between Dodge City and the Great Bend water-quality station. Again, opposing effects of evaporative concentration versus dilution by additional water would be important, with the latter factor becoming relatively more important due to the greater annual precipitation at Great BEnd than at the stations to the west.

Rattlesnake Creek near Raymond. The western portion of Rattlesnake Creek drains alluvial sediments and dune sands overlying lower Cretaceous sandstones and shales which contain saline formation water. The major salt input to Rattlesnake Creek through the surface silts, sands, and gravels, however, is from dissolution of halite in the Salt Plain Formation. Some gypsum is also included in the Permian shales, siltstones, and sandstones containing the salt. Concentration of the waters in salt marshes results in high Na and Cl concentrations not only in low flows, but also in high flows flushing out the easily dissolved salts in surface waters and soil surfaces of the marshes.

Arkansas River near Hutchinson. The Hutchinson station is the first on the Arkansas River below the large inputs of saline water from Rattlesnake Creek and other smaller tributaries. Thus, the water quality reflects a mixture of the high Ca, SO_4 concentrations in the Arkansas River in western Kansas and high Na, Cl from halite dissolution in south-central Kansas. Average annual rainfall is higher and potential evaporation lower, which may also be of significance at Hutchinson in comparison to the more western stations.

Arkansas River at Arkansas City. Appreciably higher flow in the Arkansas River at Arkansas City than in the above stations results from drainage in areas of still higher precipitation and lower evaporation. These areas include additional sources of saline water from halite dissolution, and better quality water derived from watersheds underlain by Permian shales, siltstones, sandstones, and limestones, and some Cretaceous shales and sandstones, without halite, but containing gypsum. Although salt inputs are large between Hutchinson and Arkansas City, the dilution effect of greater quickflow and infiltration of precipitation should be more than at Hutchinson.

Neosho River near Parsons. The Neosho River at Parsons is the largest river in southeast Kansas, where average annual precipitation is the highest in the state. The drainage basin is underlain by Permian and Pennsylvanian limestones, shales, and sandstones. The only appreciable source of any dissolved constitutents in higher concentrations than that derived from calcareous rocks is the solution of gypsum in the westernmost tributary, the Cottonwood River. The relatively high rainfall and absence of saline water sources result in much more dilute water and higher average discharge than in the Arkasnas River.

PROCEDURE

Data Collection

All of the discharge and quality data, except the chemical analyses for the Smoky Hill River at Enterprise during the spring of 1978, were obtained from the yearly Water Resources Data for Kansas reports for the years 1964-1977 published by the U.S. Geological Survey. Table 1 lists the water years with chemical data during these periods at the different river stations.

Daily water samples were collected from the Smoky Hill River at Enterprise during March 9 to May 20, 1978. A weighted polyethylene bottle was dropped from the bridge, and subsamples, taken at four locations spaced evenly across the river during high flow or three at low-flow, were composited. The sample was refrigerated in the field and filtered through a 0.45 µm membrane filter within one day after being brought to the laboratory. Part of the sample was preserved with HNO_3 to give a concentration of 2 ml of acid per liter. Specific conductance was measured with a Lab-Line Model Mark IV meter and Model CD/10/B dipping epoxy conductivity cell with a cell constant near 1 cm^{-1} immediately after sample filtration. The equipment was calibrated after sample filtration. The equipment was calibrated periodically with a standard KCl solution. Conductance values were corrected to 25°C and have an estimated accuracy and precisions of ±2 and ±0.5%, respectively. Sulfate concentrations were determined turbidimetrically using a salt-acid solution in the unacidified samples. Chloride was analyzed in unacidified samples by specific ion electrode and an ionic strength buffer of Hathaway (unpublished). Both SO_4 and Cl concentrations are probably accurate to within ±4%. Cations concentrations (Ca and Na) were determined in the acidified samples with a Perkin Elmer Model 305B atomic absorption spectrophotometer and should have an accuracy of ±2%. Discharge values for the Smoky Hill River at the specific times of sample collection were obtained from unpublished records of hourly river stages and the appropriate rate curve on file in the U. S. Geological Survey offices in Lawrence.

Calculations

Concentration of river waters by evaporation from free surfaces was calculated using the in-channel hydraulic geometry of rivers in Kansas for particular discharges (Burns, 1971). The amount of concentration per unit length of channel was estimated from

$$C_2/C_1 = V_1/V_2 = (D + E)/D$$

where C_1 and C_2 are the concentrations of a dissolved constituent in the river water before and after the evaporation, respectively,

V_1 and V_2 are the volumes of water in the channel before and after the evaporation, respectively,

D is the average depth of the river in the section being considered, and E is the depth of the layer of water evaporated.

The value E was determined by

$$E = R \cdot L/L$$

where R is the evaporation rate,
L is the length of the channel section,
and S is the average velocity of the river water.

Monthly evaporation rates were estimated for different areas of Kansas using yearly rates of lake evaporation obtained from a map, which were then divided proportionately into amounts corresponding to a table of monthly rates of reservoir evaporation for selected cities (Todd, 1970).

RESULTS AND DISCUSSION

Quickflow Chemistry

Quickflow, or direct runoff, is defined by Ward (1975) as the sum of channel precipitation, surface runoff (overland and channel flow), and rapid interflow. In the Hewlett runoff mode described by Ward, overland flow usually contributes only a small portion of the runoff during peak flows, while rapid interflow is the main contributor which extends ". . . the perennial channel system into zones of low storage capacity which quickly become saturated as a result of infiltration. . ." such as, ". . . into the lower valley sides, minor depressions, swampy spots, and intermittent channels. . . . The main significance of this channel-system expansion is that the very rapid contribution of channel precipitation to quickflow is effectively increased in a directly proportional way." (Ward, 1975, p. 247-248). A large part of the interflow extending the channels can consist of water already stored in the soil mantle which is pushed through or displayed by translatory flow of infiltration-induced interflow higher up slope. The main importance of this in explaining peak flow water chemistry in rivers is that dissolved constituents would not only be derived from the surface of soils by overland flow, but also from within the soil column, including possibly large amounts of soil moisture which existed previous to the rain producing the peak flow, and thus, which had time to leach higher concentrations of constituents. Also, salts concentrated at or near the soil surface by evapotranspiration would be dissolved and transmitted largely as interflow.

Direct precipitation on river channels would dilute the concentrations of major dissolved constituents in the water because rain contains much lower concentrations of these constituents than in rivers in Kansas. For example, filtered rainwaters from Pottawatomie County during 1975-1976 had a specific conductance range of 6-30 μmho/cm, and concentration ranges in mg/l of 0.4-3 for dissolved Ca, 0.04-0.5 for Na, and 0.1-6 for the sum of SO_4 and Cl (Whittemore and Switek, 1977). The amount of dilution depends on the depth of the river during the rainstorm and the amount of rain reaching the river surface. The depth of the river changes during the storm, the rate of change depending mainly on the depth immediately previous to the storm, the amount and intensity of the rain, and the soil moisture conditions during the storm. A site for which direct precipitation would have the greatest dilution effect would be a shallow, broad river during a low flow period, especially the wide, braided channels with sand banks of many streams and rivers of western and central Kansas. Conditions under which the dilution effect of direct rain would be largest are a rain of moderate intensity falling after an extended dry period at such a rate that the soil moisture capacity would not be exceeded, resulting in little, if any, overland flow and a minimum of quick interflow. A rainstorm of large areal extent continuing for a day and stationary or moving only very slowly toward the east could possibly dilute waters in shallow tributaries to rivers by an estimated factor of two from direct precipitation. An example would be a storm dropping 0.1 foot of precipitation over broad channels of 0.1 foot average depth.

The larger the river, the greater the average channel depth and the smaller the dilution effect of direct precipitation. Even in the upstream reaches where the river or its tributaries have shallow channels, some increased flow could result from rapid interflow in the immediate vicinity of the channel, including the permeable alluvium itself, and thus increase the depth of the channel. However, extension of the perennial channels according to the Hewlett runoff model would expand the channel system and increase the contribution of direct precipitation to runoff. Storms with greater amounts of rainfall than 0.1 foot would appreciably increase rapid interflow and thus channel depth. Given optimum conditions, the maximum dilution effect of direct precipitation at river sites treated in this study is not expected to be greater than 50% (thereby reducing solute concentrations by one-third). This could occur only at the smaller and shallower river stations, i.e., the Saline River at Russell, South Fork Solomon River at Osborne, the Arkansas River from Coolidge to Great Bend, and Rattlesnake Creek near Raymond. Most of the time, direct precipitation would probably dilute most rivers in Kansas by less than 10%.

The chemistry of peak flows is thus controlled mainly by the removal of dissolved constituents from soils by rapid interflow and to a smaller degree by varying degrees of dilution by direct precipitation. Generally, the greater the discharge at a given river site, the lower the total dissolved solids (TDS). An example of this is shown in Figure 2 for the Smoky Hill River at Enterprise. The larger the rainstorm or snowmelt, the greater the amount of flushing out of soil moisture with higher TDS which is then followed by rapid interflow of lower TDS.

The average chemistry of the lowest TDS concentrations and highest discharges reached for the different river sites during 1964-1977 considered in this study are given in Tables 2 and 3. The number of values selected for averaging depended mainly on the number of observations of low TDS and high discharge relative to the total number of observations

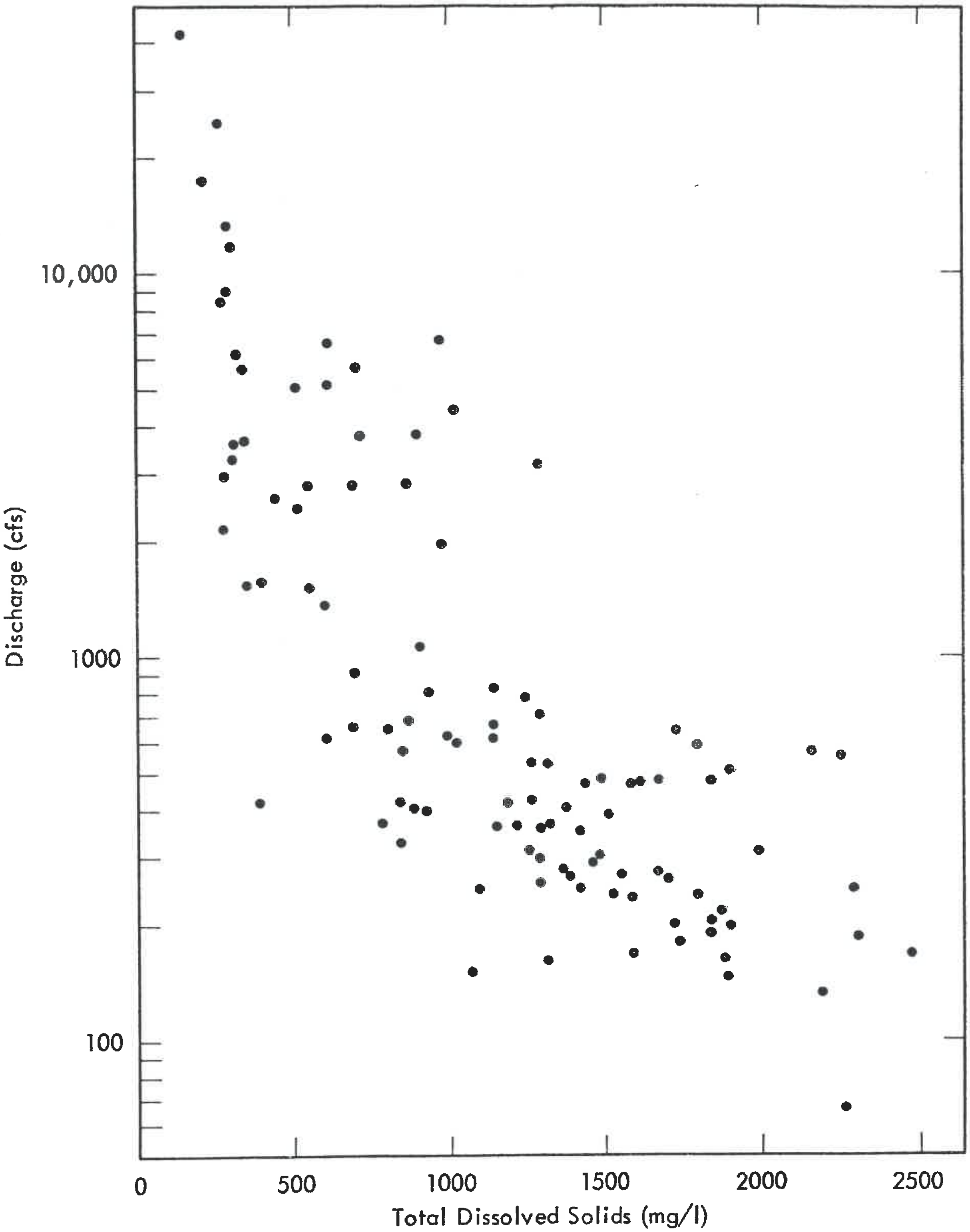


Figure 2. Discharge Versus Total Dissolved Solids for the Smoky Hill River at Enterprise, 1970-1977.

Table 2. Average Chemical Data for the Lowest Total Dissolved Solids (TDS) and Highest Discharges at River Stations in the Kansas River Basin

River Station	Averaging Basis[a]	Discharge (cfs)	Sp.C.[b] (μmho/cm)	TDS (mg/l)	Ca (mg/l)	Na (mg/l)	SO_4 (mg/l)	Cl (mg/l)	$\frac{Na}{Na + Ca}$	$\frac{Cl}{Cl + SO_4}$
Saline R.	T-5	2070	428	268	59	16	50	24	.218	.329
near Russell	D-4	3080	529	334	72	22	80	36	.222	.300
S. Fork Solomon	T-4	587	318	223	51	9.2	35	10	.151	.214
R. at Osborne	D-5	1360	486	330	68	23	74	32	.214	.264
Solomon R.	T-9	6950	213	146	30	7.4	14	11	.208	.445
at Niles	D-7	8330	228	161	37	8.6	16	12	.178	.436
Smoky Hill R.	T-8	14,780	302	194	41	17	29	19	.287	.391
at Enterprise	D-6	22,620	330	210	46	16	31	21	.246	.405
Republican R.	T-6	4830	216	150	28	7.5	13	7.4	.208	.381
at Concordia	D-8	5480	278	182	36	9.8	24	10	.208	.336
Big Blue R.	T-6	7200	143	109	18	4.9	14	4.5	.214	.247
near Oketo	D-5	9020	140	113	17	5.0	15	3.9	.222	.208
Kansas R.	T-9	24,890	302	193	43	12	21	15	.210	.409
at Wamego	D-9	31,680	384	250	47	19	46	24	.265	.367

[a] Averaging basis is either TDS (T) or discharge (D) followed by the number of samples used in the average.
[b] Specific conductance at 25°C.

Table 3. Average Chemical Data for the Lowest Total Dissolved Solids (TDS) and Highest Discharges at River Stations in the Arkansas River Basin

River Station	Averaging Basis[a]	Discharge (cfs)	Sp.C.[b] (μmho/cm)	TDS (mg/l)	Ca (mg/l)	Na (mg/l)	SO4 (mg/l)	Cl (mg/l)	$\frac{Na}{Na + Ca}$	$\frac{Cl}{Cl + SO_4}$
Arkansas R. near Coolidge	T-4	3920	833	630	88	54	292	16	.344	.058
	D-3	5090	891	673	96	65	351	19	.379	.057
Arkansas R. at Dodge City	T-3	5790	587	396	67	35	158	13	.335	.079
	D-2	9230	630	430	70	40	188	14	.354	.064
Arkansas R. at Great Bend	T-7	7760	441	296	55	21	86	12	.265	.176
	D-4	13,220	445	309	57	21	105	7.9	.252	.145
Rattlesnake Cr. near Raymond	T-2	276	2180	1200	62	372	64	562	.855	.898
	D-2	333	3150	1745	66	578	93	865	.894	.864
Arkansas R. near Hutchinson	T-8	7620	404	248	36	36	37	48	.500	.648
	D-8	10,660	455	289	44	38	67	46	.482	.540
Arkansas R. at Arkansas City	T-8	22,220	294	178	22	27	25	37	.554	.600
	D-8	24,320	307	188	23	29	29	38	.556	.582
Neosho R. near Parsons	T-7	23,500	151	114	22	11	11	7.6	.203	.428
	D-7	23,930	159	115	23	13	13	8.1	.209	.422

[a] Averaging basis is either TDS (T) or discharge (D) followed by the number of samples used in the average.
[b] Specific conductance at 25°C.

during the period; the greater the number of each, the greater the number of values used in the averages. In general, the farther east the river site, the lower the concentrations of dissolved constituents, reflecting the higher precipitation and lower evaporation proceeding from western to eastern Kansas. The climates with higher rainfalls have soils through which more water flows and which have less time to accumulate salts as a result of evaporation. Also, the higher rainfalls and thus quickflow discharges dilute mineralized baseflow more. For a few river stations, there are moderate differences between averages based on the lowest TDS observations and those based on highest discharges. These indicate that there could be differences in source areas of quickflow to the river, the type of high discharge event, the weather previous to the high flow, and the time at which the sample was taken during the high flow period. Further explanations for the variations are included in later sections of this report.

In the Kansas River basin stations and the Neosho River at Parsons, the weight ratio Na/(Na + Ca) for quickflow is about 0.20 ±0.05, while the Cl/(Cl + SO_4) is higher and varies more (0.3 ±0.1). Higher values of Na/(Na + Ca) and very low Cl/(Cl + SO_4) in the quickflow of the Arkansas River from Coolidge to Great Bend are probably partially derived from the baseflow diluted by the runoff at the beginning of the storm, and partly from the leaching of near surface sediments of the broad alluvial valley. Salts could be concentrated in these sediments by evapotranspiration after mineralized groundwater was drawn upwards by capillary action or spread on the surface by irrigation. The original high Na/(Na + Ca) and very low Cl/(Cl + SO_4) were likely acquired from the solution of evaporite deposits (mainly sulfate minerals) in the drainage basins of tributaries to the Arkansas River in eastern Colorado. It is noted that Na/(Na + Ca) decreases and Cl/(Cl + SO_4) increases in high flow of the Arkansas River proceeding eastward from Coolidge to Great Bend, showing the decreased influence of the main dissolved solids source. The high Na/(Na + Ca) and Cl/(Cl + SO_4) for quickflow in Rattlesnake Creek, and the Arkansas River downstream from the junction with the tributary, represent salts flushed out of areas where halite is being dissolved in underlying bedrock. Salt marshes along the valley of Rattlesnake Creek, in which dissolved constituents are concentrated and precipitated at the surface by evaporation, are a source of great amounts of salts in surface runoff.

Baseflow Chemistry

Baseflow is the sum of groundwater flow and delayed interflow. During extended dry periods in Kansas, baseflow consists almost entirely of groundwater flow except where reservoir outflows provide an appreciable contribution to river flow. The chemistry of baseflow during minimum flows thus usually reflects the chemistry of groundwater discharging to the river. In general, the lower the discharge at a given river site, the higher the TDS (Figure 2). The lowest flows, however, do not necessarily give the highest TDS. The amount of previous groundwater recharge providing hydrostatic pressure to push out greater amounts of deeper, more saline groundwater under the river may explain this for many stations (see the later section on cyclic variations in river water chemistry). In addition to the groundwater influence on baseflow quality, evaporation from the river water surface can concentrate the dissolved constituents and change the Na/Ca by precipitation of $CaCO_3$.

The two main factors controlling the chemistry of groundwater flow to rivers are the geology and the climate. Groundwaters with the greatest TDS either have dissolved evaporite minerals (halite, gypsum, anhydrite) or are near surface, saline formation waters in permeable strata. Shallow bedrock in most areas of Kansas contains some carbonates, either as limestone or dolomite strata, or as calcite in shales or sandstones, thus groundwater is usually at least hard, Ca, Mg, HCO_3 water. Given areas of similar bedrock containing either evaporite minerals or saline formation waters, the greater the precipitation, generally the lower the total dissolved solids in the near surface groundwater. The larger amounts of infiltration recharging the aquifers have a shorter residence time in which to dissolve soluble minerals before discharging to streams, and also dilute existing groundwater more than in dry areas.

The average chemistry of the 10 highest TDS values and 10 lowest discharge observations for which chemical data are available are shown in Tables 4 and 5. Except for the Neosho River at Parsons, the weight ratios of Na/(Na + Ca) are all much higher and vary from station to station more for baseflow than quickflow. The Cl/(Cl + SO_4) values for baseflow also vary widely, and are all higher than for quickflows in the Kansas River basin with the exception of the Republican River at Concordia. At the Arkansas River basin stations the Cl/(Cl + SO_4) values are either the same, higher, or lower than for quickflow.

Very high TDS, Na/(Na + Ca), and Cl/(Cl + SO_4) of the Saline River at Russell are derived from saline formation waters of the Dakota Formation, which were originally seawater, and which have mixed with varying amounts of fresh groundwater before seeping to streams. In contrast, TDS and both constituent ratios at the South Fork of the Solomon River at Osborne are much lower and reflect groundwaters from shales, chalk, and limestone with traces of gypsum. Baseflows at both sites undergo some concentration by evaporation of water from the river surface. Saline waters from the Dakota Formation influence the baseflow chemistry of the Solomon River at Russell because there are larger upstream flows and greater amounts of infiltrating precipitation to dilute the saline seepage. Water in the Smoky Hill River at Enterprise is a mixture of the Saline and Solomon Rivers and the upstream part of the Smoky Hill River, but contains higher concentrations of Na and Cl and a lower Na/Cl (0.661 - 0.668) than for simple mixtures of the tributaries. This results from a large input of saline water derived from the solution of halite (Na/Cl = 0.649) east of Salina, and entering the river through the alluvium between New Cambria and Solomon. Groundwater

Table 4. Average Chemical Data for the Ten Highest Total Dissolved Solids (TDS) and Ten Lowest Discharges at River Stations in the Kansas River Basin

River Station	Averaging Basis	Discharge (cfs)	Sp.C.[a] (μmho/cm)	TDS (mg/l)	Ca (mg/l)	Na (mg/l)	SO$_4$ (mg/l)	Cl (mg/l)	$\frac{Na}{Na + Ca}$	$\frac{Cl}{Cl + SO_4}$
Saline R. near Russell	TDS	10.6	11,080	7010	188	2200	1080	3130	.920	.741
	Dis.	2.8	10,140	6380	201	1960	1030	2800	.906	.730
S. Fork Solomon R. at Osborne	TDS	181	1640	1110	196	119	385	168	.379	.304
	Dis.	2.5	1050	682	115	80	184	92	.412	.321
Solomon R. at Niles	TDS	68	2660	1560	124	395	268	504	.760	.644
	Dis.	32	2110	1250	103	310	212	386	.738	.638
Smoky Hill R. at Enterprise	TDS	262	3720	2200	161	590	335	892	.785	.726
	Dis.	124	2970	1760	148	434	289	650	.743	.689
Republican R. at Concordia	TDS	332	1130	727	123	84	183	84	.406	.315
	Dis.	88	962	623	103	76	151	69	.427	.314
Big Blue R. near Oketo	TDS		752	472	83	54	79	46	.396	.369
	Dis.	25	611	382	66	45	46	45	.408	.495
Kansas R. at Wamego	TDS	1150	1460	891	109	160	179	234	.597	.566
	Dis.	409	1140	693	86	121	126	171	.573	.561

[a] Specific conductance at 25°C.

Table 5. Average Chemical Data for the Ten Highest Total Dissolved Solids (TDS) and Ten Lowest Discharges at River Stations in the Arkansas River Basin

River Station	Averaging Basis	Discharge (cfs)	Sp.C.[a] (µmho/cm)	TDS (mg/l)	Ca (mg/l)	Na (mg/l)	SO_4 (mg/l)	Cl (mg/l)	$\frac{Na}{Na + Ca}$	$\frac{Cl}{Cl + SO_4}$
Arkansas R.	TDS	47	4900	4490	416	626	2520	186	.601	.069
near Coolidge	Dis.	3.6	4430	4190	401	584	2560	202	.593	.076
Arkansas R.	TDS	174	3850	3160	301	426	1760	132	.586	.070
at Dodge City	Dis.	2.8	1140	794	105	94	337	32	.459	.090
Arkansas R.	TDS	237	2930	2310	257	329	1340	115	.562	.079
at Great Bend	Dis.	6.3	1200	811	103	115	358	66	.527	.159
Rattlesnake Cr.	TDS	9.6	13,980	8460	156	2980	536	4560	.950	.895
near Raymond	Dis.	0.8	8570	4900	97	1710	327	2600	.944	.884
Arkansas R.	TDS	158	4640	2760	153	802	440	1150	.835	.722
near Hutchinson	Dis.	72	4060	2390	125	704	313	1040	.845	.768
Arkansas R.	TDS	586	3090	1960	152	475	404	662	.741	.597
at Arkansas City	Dis.	265	2530	1520	116	384	225	565	.768	.717
Neosho R.	TDS	616	657	414	92	25	84	34	.215	.288
near Parsons	Dis.	14.7	468	298	59	19	48	30	.242	.378

[a] Specific conductance at 25°C.

from sands and gravels, and shales and limestones containing traces of gypsum mainly controls the chemistry of baseflow in the Republican River at Concordia, although evaporative concentration of dissolved constituents could substantially increase TDS during hot, dry periods. The chemistry of the Republican River at this site is fairly similar to that of the South Fork of the Solomon at Osborne. Low flows in the Big Blue River are also somewhat affected by a small amount of gypsum in shale and limestone, but are more dilute due to a more humid climate in the watershed, than in the Republican River at Concordia and the South Fork of the Solomon at Osborne, although the chemical ratios are similar. The Kansas River at Wamego has baseflows with relatively high TDS for their volume, indicating the strong influence of the saline groundwater seeps in the Saline, Solomon, and Smoky Hill Rivers.

Baseflows of the Arkansas River from Coolidge to Great Bend have high TDS, moderately high Na/(Na + Ca), and extremely low Cl/(Cl + SO_4) derived originally from solution of sulfate evaporites in bedrock in southeastern Colorado. The very high Na/Cl ($\sim$ 3 at Coolidge and Dodge City) probably results from the solution of sodium sulfates associated with the gypsum, but may also be partially derived from cation exchange of Ca for Na on clays. Travel of the water through southeast Colorado, (including holding in the John Martin reservoir), and southwest Kansas, areas with high potential evaporation rates, and use of the water for irrigation results in appreciable concentration by evapotranspiration. This probably increases Na/(Na + Ca) during dry periods by precipitation of $CaCO_3$ (see the following section on the evaporation-crystallization process). Interchange of water between alluvium and river, depending on river stage, and general downstream groundwater flow in the alluvium has spread the highly mineralized water, originally derived from southeastern Colorado, far down the Arkansas river valley in western Kansas. Recharge of the alluvial aquifer by local waters in Kansas travelling through soils, sediments, and rock without highly soluble minerals dilutes the groundwater and thus, the baseflow, and lowers Na/(Na + Ca) and Na/Cl, and increases Cl/(Cl + SO_4). Increasing influence of the local recharge can be seen in Table 5 proceeding downstream from Coolidge to Great Bend.

The extremely high TDS, Na/(Na + CA) and Cl/(Cl + SO_4) in minimum flows of Rattlesnake Creek near Raymond result mainly from subsurface solution of halite followed by evaporative concentration in the river and salt marshes. Farther upstream in the basins of Rattlesnake Creek there may be a smaller source of saline formation waters from Lower Cretaceous rocks. The Na/Cl ratio of 0.654 - 0.658 verifies that the major source of these constituents is halite solution (Na/Cl = 0.649). The Arkansas River below its juction with Rattlesnake Creek reflects the strong influence of this and other saline tributaries and seeps. The Na/(Na + Ca) remains appreciably higher than the Cl/(Cl + SO_4) in the river as a result of mixing with the water from the western portions of the river where Cl/(Cl + SO_4) is very low. Baseflow at Arkansas City has a higher TDS than the Kansas River at Wamego, even when equivalent discharges are considered.

The Neosho River near Parsons has baseflows which are much more dilute than at any station on the Arkansas River, indicating the effect of higher rainfall, which causes greater recharge and, therefore, dilution of aquifers, and lower evaporation, which decreases the importance of evaporative concentration. Some gypsum in shales and limestone of the westernmost portion of the basin, specifically the westernmost part of the Cottonwood River watershed, causes the low Na/(Na + Ca) and Cl/(Cl + SO_4) in the baseflow.

Evaporation-Crystallization Process

Appreciable evaporative concentration of waters not only increases the TDS of waters, but may also alter their chemistry by supersaturating the water with respect to certain minerals, causing selective precipitation of particular constituents. Most commonly this occurs when the waters are saturated with respect to calcite, a condition existing for most Kansas surface and ground waters. Although the Ca concentration of waters can continue to increase during evaporative concentration as a consequence of higher ionic strength and ion pairing with SO_4, some Ca can be removed by crystallization of calcite when the water is sufficiently supersaturated with respect to this mineral. Because Na is not removed by precipitation, its increases at a faster rate than Ca, thus increasing Na/(Na + Ca). This becomes detrimental in that the sodium hazard of irrigation waters to soils increases, as the hazard is largely based on the relative amount of Na in comparison with Ca and Mg.

The greatest effect of concentration by evaporation at a particular site is during the summer months when evaporation rates are highest, as shown for the Smoky Hill River and Kansas River in Table 6. The in-channel hydraulic properties of the river station, however, are actually more important in terms of the percent of volume evaporated per channel mile than the time of year. For example, the Smoky Hill River between McAllaster and Elkader concentrates at a faster rate in January on the average, than between Enterprise and Wamego, taking into account the different evaporation rates between the two sections. At a particular river site varying discharge causes varying depths, thus the amount of evaporative concentration changes with discharge (Table 6). Table 7 gives the total percent evaporation and the concentration of the river water occurring between stations in the Smoky Hill and Kansas River. Table 8 shows the data and results of the calculations of evaporative concentration for sections of the Arkansas River. The concentration factor is for the average depth and thus average discharge between the two stations.

To determine the total evaporative concentration for two consecutive sets of river stations, the product of the two concentration factors could be used where there was no new addition of water to the river other than surface water from tributaries. Most water added from tributaries in the Kansas River basin would have undergone evaporation at a rate approaching the total evaporation to that point in the river,

Table 6. Data Used for and Results of Calculations of Free Surface Evaporation per River Mile of the Smoky Hill River and Kansas River Between Different Stations. Stations are listed in upstream to downstream order. The symbols Q50 and Q80 refer to channel flows exceeded 50 and 80 percent of the time, respectively. (Calculations and references are listed in the section on procedure.)

		Average Evaporation Rate	River Channel Characteristics				Percent River Volume Evaporated per Mile			
			Average Depth (ft)		Average Velocity (ft/sec)		Q50		Q80	
Station 1	Station 2	(in/yr)	Q50	Q80	Q50	Q80	January	July	January	July
McAllaster	Elkader	60	0.3	0.15	1.0	0.8	0.049	0.54	0.12	1.35
Elkader	Arnold	61	0.38	0.2	1.2	0.8	0.032	0.36	0.092	1.02
Cedar Bluffs	Ellis	62	0.45	0.3	1.0	0.8	0.033	0.37	0.062	0.69
Ellis	Russell	61	0.53	0.3	1.3	1.0	0.021	0.24	0.049	0.55
Russell	Ellsworth	59	0.75	0.45	1.4	1.1	0.014	0.15	0.030	0.32
Langley	Lindsborg	57	1.3	0.95	1.3	1.1	0.009	0.091	0.014	0.15
Lindsborg	Mentor	56	1.4	0.9	1.3	1.1	0.008	0.083	0.015	0.15
Mentor	Enterprise	55	1.7	1.1	1.6	1.3	0.005	0.055	0.010	0.11
Enterprise	Wamego	52	2.4	1.7	1.9	1.6	0.003	0.031	0.005	0.053

Table 7. Total Evaporation and Evaporative Concentration Factors for Sections of the Smoky Hill River and Kansas River. Stations are listed in upstream to downstream order. The symbols Q_{50} and Q_{80} refer to channel flows exceeded 50 and 80 percent of the time, respectively.

		Channel Distance Between Stations	Percent River Volume Evaporated Between Stations				Evaporative Concentration Factor Between Stations			
			Q_{50}		Q_{80}		Q_{50}		Q_{80}	
Station 1	Station 2	(mi)	January	July	January	July	January	July	January	July
McAllaster	Elkader	30	1.5	16	3.7	40	1.02	1.20	1.04	1.68
Elkader	Arnold	54	1.7	19	4.9	55	1.02	1.24	1.05	2.22
Cedar Bluffs	Ellis	10	0.33	3.7	0.62	6.9	1.003	1.04	1.006	1.07
Ellis	Russell	57	1.2	14	2.8	31	1.01	1.16	1.03	1.46
Russell	Ellsworth	53	0.74	8.0	1.6	17	1.007	1.09	1.02	1.21
Langley	Lindsborg	40	0.36	3.6	0.56	5.9	1.004	1.04	1.006	1.06
Lindsborg	Mentor	41	0.33	3.4	0.62	6.3	1.003	1.04	1.006	1.07
Mentor	Enterprise	58	0.29	3.2	0.58	6.2	1.003	1.03	1.006	1.07
Enterprise	Wamego	87	0.26	2.7	0.43	4.6	1.003	1.03	1.004	1.05

Table 8. Data Used for and Results of Calculations of Free Surface Evaporation from the Arkansas River during July for Flows Exceeded 80 Percent of the Time. Stations are listed in upstream to downstream order.

Station 1	Station 2	Average Evaporation Rate (in/yr)	River Channel Characteristics Average Depth (ft)	River Channel Characteristics Average Velocity (ft/sec)	Channel Distance Between Stations (mi)	Percent River Volume Evaporated Between Stations	Evaporative Concentration Factor Between Stations
Syracuse	Garden City	61	0.4	1.1	57	20	1.25
Garden City	Dodge City	62	0.55	1.35	54	12	1.14
Dodge City	Kinsley	63	0.75	1.7	50	6.6	1.07
Kinsley	Great Bend	62	0.8	1.65	47	6.0	1.06
Great Bend	Wichita	58	0.9	1.4	110	14	1.16
Wichita	Arkansas City	56	1.03	1.45	62	6.3	1.07

because the tributaries flow generally parallel to each other, and the larger the main river, the larger are most of the tributaries. This would not be as true in the Arkansas River basin, but in western Kansas, inflow from tributaries to the Arkansas is small. However, because there is new addition of groundwater from the alluvium directly to the low flow of rivers, an adjustment to each concentration factor between stations must be made. In many areas the groundwater discharge to a river is probably appreciably greater than the loss of flow by evaporation. If the percentage of the flow added by groundwater remained constant proceeding downstream, then its volume influence would increase relative to that caused by evaporation, which decreases in percentage effect downstream mainly due to the increase in river depth. Assuming a doubling of the river flow during a 50 mile channel section, if the amount of groundwater inflow and tributary flow causing the increase were equal, then for evaporative losses approximately equal in volume to the groundwater discharge, the average river depth would have to be about 0.5 feet in western or central Kansas during July. At shallower river depths, evaporation would have a greater volume effect on baseflow than groundwater and vice versa. A few stretches of rivers, such as the Arkansas between Coolidge and Garden City, lose water to the alluvium. Problems would arise in evaporative concentration calculations at very low flows which may be entirely lost in sections of losing rivers and thus not be available at the surface for evaporation.

Evaporation of irrigation waters can also appreciably add to the effective net concentration of baseflow, both by return flows to the river or by infiltration into an alluvial aquifer discharging to the river. This is particularly important in western reaches of the Arkansas River valley where large amounts of irrigation waters are both withdrawn from wells in the alluvial aquifer and diverted by the Amazon Ditch near Garden City.

Comparison of Quickflow and Baseflow Chemistry

When the quickflow and baseflow chemistry of the rivers are compared, it is apparent that at all stations the weight ratio Na/(Na + Ca) increases from both high to low discharge (Figures 3 and 4). These changes are due primarily to differences between the chemistry of soil moisture and groundwater and to the evaporation-crystallization process. Where the variations in Na/(Na + Ca) are very large, as for the Saline, Solomon, Smoky Hill, and Kansas River, the soil moisture versus groundwater composition would be the most important control, because the evaporation-crystallization process can only account for smaller changes in Kansas. The magnitude of changes which might be expected for predominant control by the latter process occur in the Arkansas River basin, especially in western Kansas and Rattlesnake Creek.

The ratio Cl/(Cl + SO_4) can be used in many cases to determine whether a difference between soil moisture and groundwater chemistry, or the evaporation-crystallization process is more important in controlling the change in Na/(Na +Ca) from quickflow to baseflow. If the

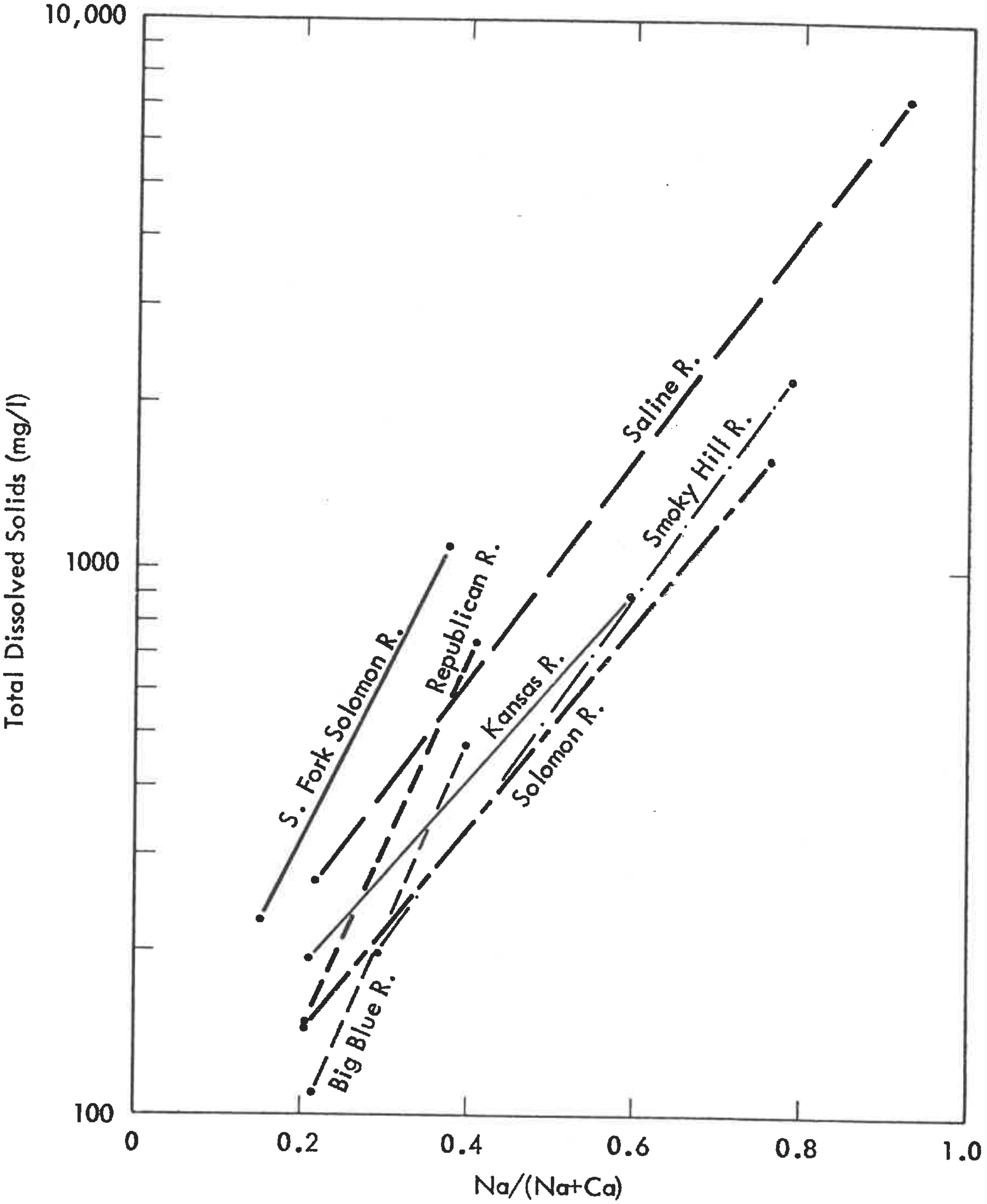


Figure 3. Comparison of Na/(Na + Ca) for the Highest and Lowest Total Dissolved Solids in Rivers of the Kansas River Basin. The points are the averages from Tables 2 and 4.

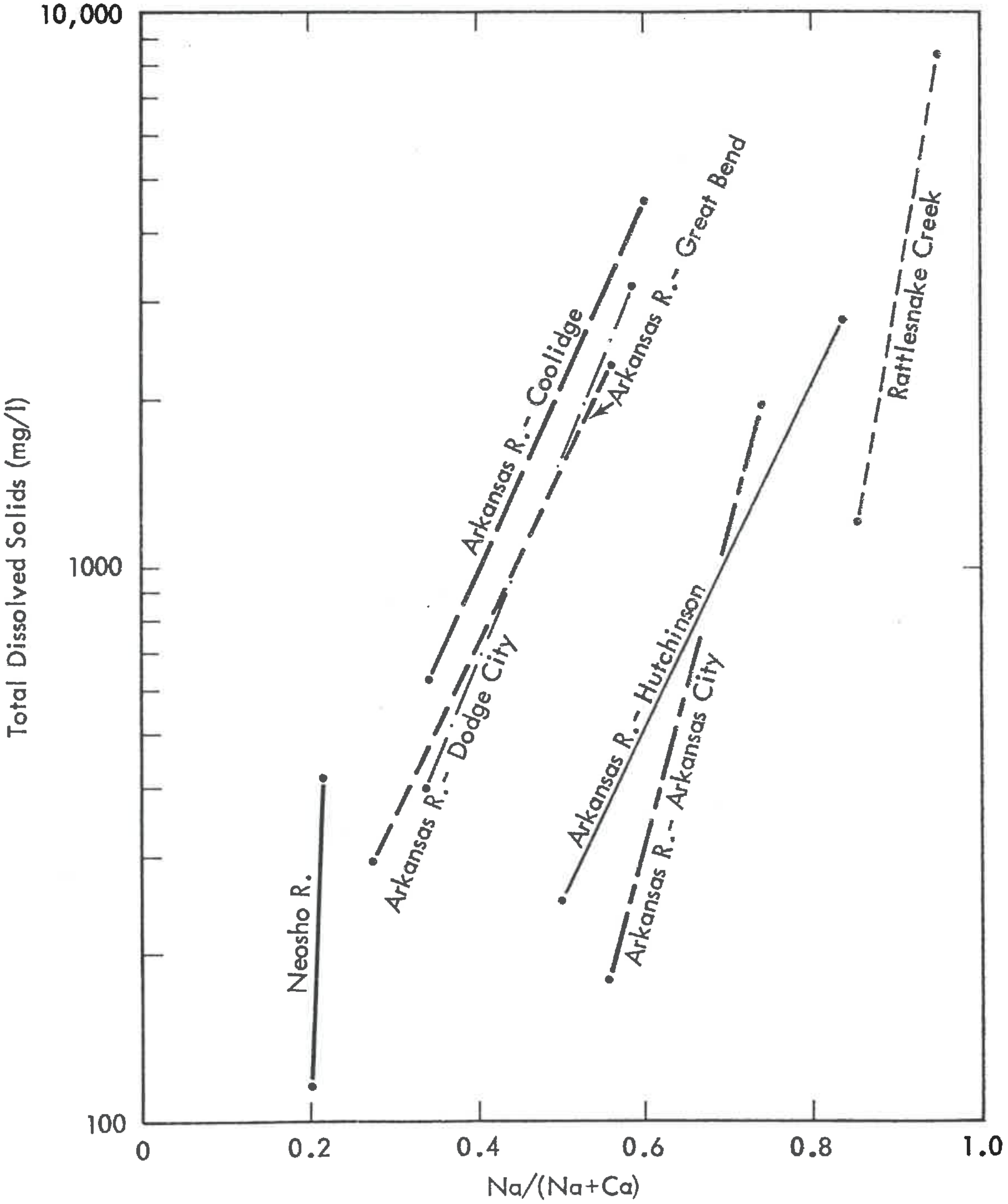


Figure 4. Comparison of Na/(Na + Ca) for the Highest and Lowest Total Dissolved Solids in Rivers of the Arkansas River Basin. The points are the averages from Tables 3 and 5.

evaporation-crystallization process is more important, $Cl/(Cl + SO_4)$ will not change much because both of these constituents are not precipitated (unless gypsum sauration is reached), or appreciably altered in concentration by ion exchange. The only river station with waters coming close to saturation with respect to gypsum is the Arkansas River at Coolidge during only the lowest flows. The amount of gypsum which might be precipitated there, however, does not appear to be enough to noticeably affect $Cl/(Cl + SO_4)$. Thus, if $Cl/(Cl + SO_4)$ changes appreciably, it indicates that a difference in soil moisture and groundwater chemistry is the major control on variation of Na/(Na + Ca) in rivers.

In the Kansas River basin, the $Cl/(Cl + SO_4)$ varies noticeably at all river stations except the South Fork of the Solomon at Osborne and the Republican River at Concordia (Figure 5), indicating chemical differences between soil moisture and groundwater as the major factor. The change in Cl/(Cl + SO4) for the two rivers which are the exceptions are smaller, suggesting either that the evaporation-crystallization process and the soil moisture-groundwater controls may be relatively closer in importance, or the differences between soil moisture and groundwater compositions are small. Unlike all of the other sites in the Kansas River watershed, the Republican River at Concordia shows a decrease in $Cl/(Cl + SO_4)$ with increasing TDS or decreasing discharge.

In the Arkansas River basin, most of the river stations studied display little change in $Cl/(Cl + SO_4)$ (Figure 6), suggesting that the evaporation-crystallization process could be important in controlling changes in Na/(Na + Ca). Differences in the $Cl/(Cl + SO_4)$ for high and low discharges (Tables 3 and 5) for two of the Arkansas River stations, Hutchinson and Arkansas City, are substantially greater than for high and low TDS (Figure 6). Different sources of water within the Arkansas River basin may be the explanation for this. For the highest discharges, drainage would probably come from a large portion of the Arkansas River basin thereby mixing waters with both the low $Cl/(Cl + SO_4)$ from seeps and tributaries such as Rattlesnake Creek in south-central Kansas. The lowest discharges would be derived most often from alluvial aquifers near Hutchinson or Arkansas City, for during dry conditions the contributions to flow farther upstream in even more arid areas would be very small. Thus, the $Cl/(Cl + SO_4)$ would be higher in the lowest discharges, reflecting the influence of high values associated with the solution of halite. Therefore, the high-low discharge data shows the greater change in $Cl/(Cl + SO_4)$ for the Hutchinson and Arkansas City stations as a result of different source areas for the water. The data used to calculate the high TDS averages for these two stations vary considerably, also indicating different water sources; most often the more local influence of high $Cl/(Cl + SO_4)$ waters in predominant, but occasionally the volume of waters of high TDS and low $Cl/(Cl + SO_4)$ farther upstream becomes important enough to decrease the $Cl/(Cl + SO_4)$ at Hutchinson and Arkansas City to as low as 0.37. Lowest TDS may be derived either from local or widespread events, thus, again the $Cl/(Cl + SO_4)$ represents a mixture of values from different sources. Therefore, the changes in $Cl/(Cl + SO_4)$ are smaller for the high-low TDS averages than for the high-low discharge averages due to a mixture of sources versus different sources of the waters, respectively, in the Arkansas River at Hutchinson and Arkansas City.

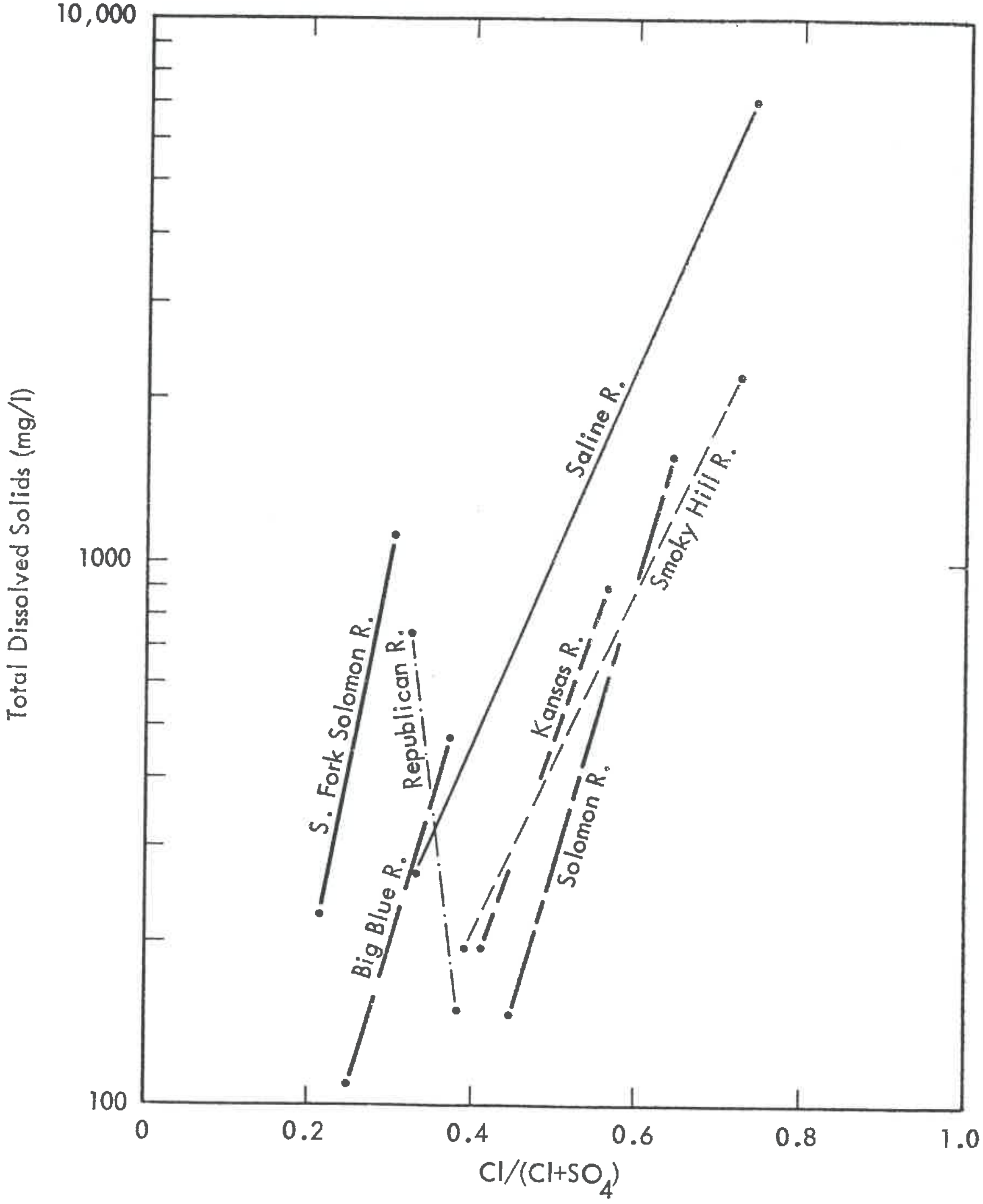


Figure 5. Comparison of $Cl/(Cl + SO_4)$ for the Highest and Lowest Total Dissolved Solids in Rivers of the Kansas River Basin. The points are the averages from Tables 2 and 4.

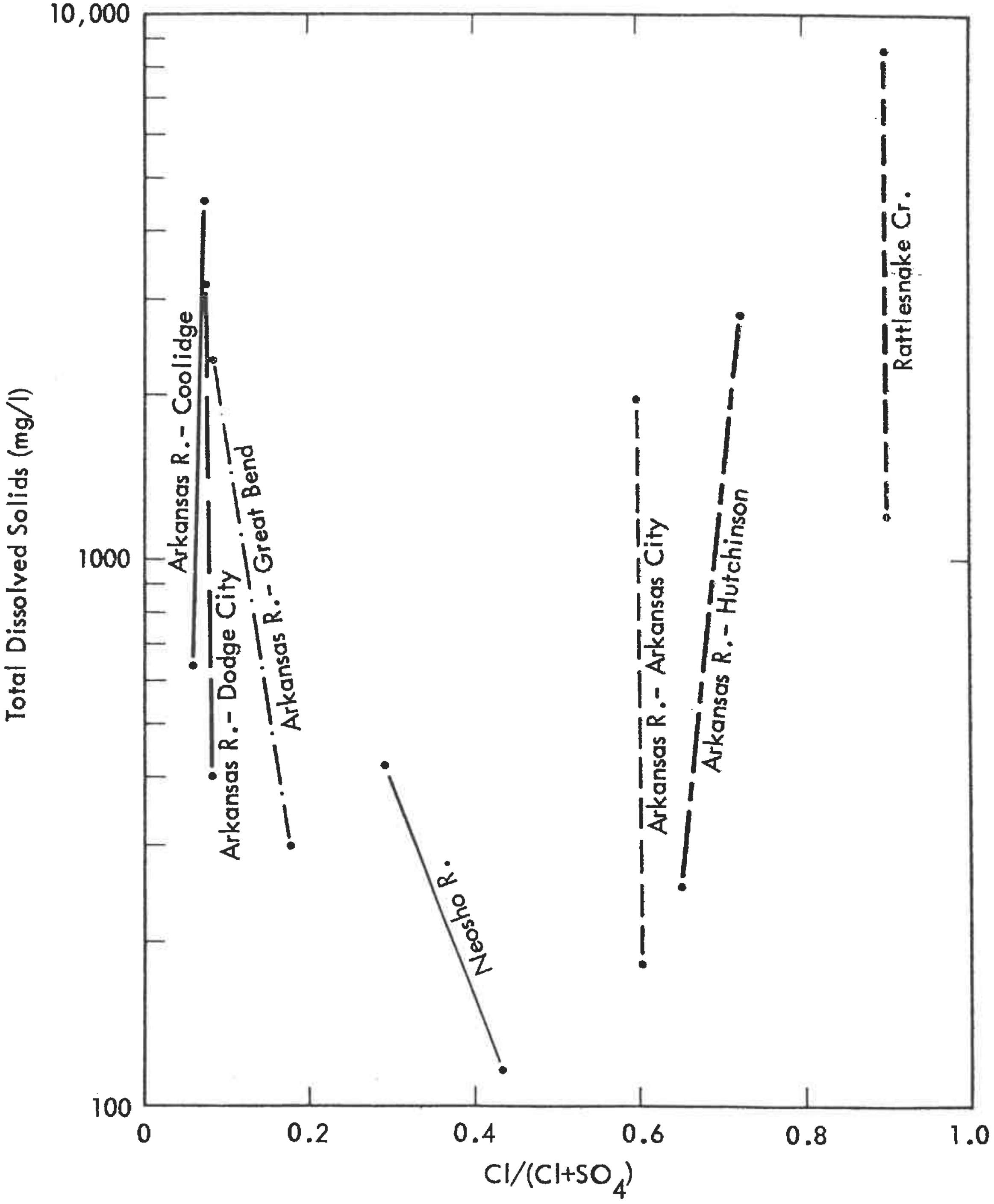


Figure 6. Comparison of Cl/(Cl + SO_4) for the Highest and Lowest Total Dissolved Solids in Rivers of the Arkansas River Basin. The points are the averages from Tables 3 and 5.

The other river in the Arkansas River basin with a substantial change in Cl/(Cl + SO_4) is the Neosho River near Parsons. Here Cl/(Cl + SO_4) decreases rather than increases with increasing TDS (Figure 6) or decreasing discharge (Tables 3 and 5). In contrast to the Arkansas River stations at Hutchinson and Arkansas City, the change is greater for the high-low TDS averages. The only source of high TDS waters in the Neosho River is in the westernmost part of the watershed, specifically the western section of the Cottonwood River basin where groundwaters dissolve gypsum present in the bedrock. The rest of the Neosho basin is underlain by limestone, shale, and sandstone without appreciable amounts of evaporites or saline formation waters. During dry periods when the lowest flows would occur, the discharge from the westernmost part of the watershed would be only a small part of the total near Parsons, not only due to the smaller source area, but also because it is in the driest part of the basin. During the highest flows a very large portion of the total watershed area of the Neosho River would be contributing to flow, reflecting mainly the chemistry of the non-gypsiferous area. The waters with lowest TDS would also drain largely from the non-gypsiferous areas, indeed, the values used to compute this average were essentially the same observations as those used in the highest discharge calculation. Thus, the Cl/(Cl + SO_4) values for low TDS, and high and low discharge averages range only from 0.378 to 0.428, while the high TDS average, indicating noticeable drainage from the gypsum bearing area, is 0.288.

Cyclic Variations in River Water Chemistry

Variations in river water quality are very great in Kansas as shown by the previous discussion. Although the general inverse relationship between discharge and TDS has been recognized before in Kansas (Durum, 1953; Jordon et al., 1964; Mundorff and Waddell, 1966), the more complex, cyclical nature of the variations has not been described.

Two types of cyclic relationships between discharge and water chemistry have been observed in rivers of Kansas. A flushing-dilution cycle follows a counterclockwise loop when discharge is plotted versus specific conductance or TDS. A dilution-groundwater discharge cycle follows a clockwise loop on a similar graph. Both of these cycles can occur at a single station of a river, although at different flow ranges.

Examples of both cyclic relationships are shown in Figure 7 for the Smoky Hill River. Flushing-dilution cycles occurred at lower ranges of discharges for two short storms during late March and early April, 1976. The first increases in discharge from the storms were either accompanied by only small decreases in specific conductance, as in the first cycle, or by small increases in conductance, as in the second loop. This is explained by flushing of the water in the river channel producing a lag effect and also, by flushing of very soluble salts accumulated by evapotranspiration in soils and unsaturated alluvium. Specific conductance then decreased rapidly as more dilute quickflow reached the river station, and continued to decrease for a short period after discharge began to fall. The specific conductance then increased as groundwater inflow again became more important in the river flow.

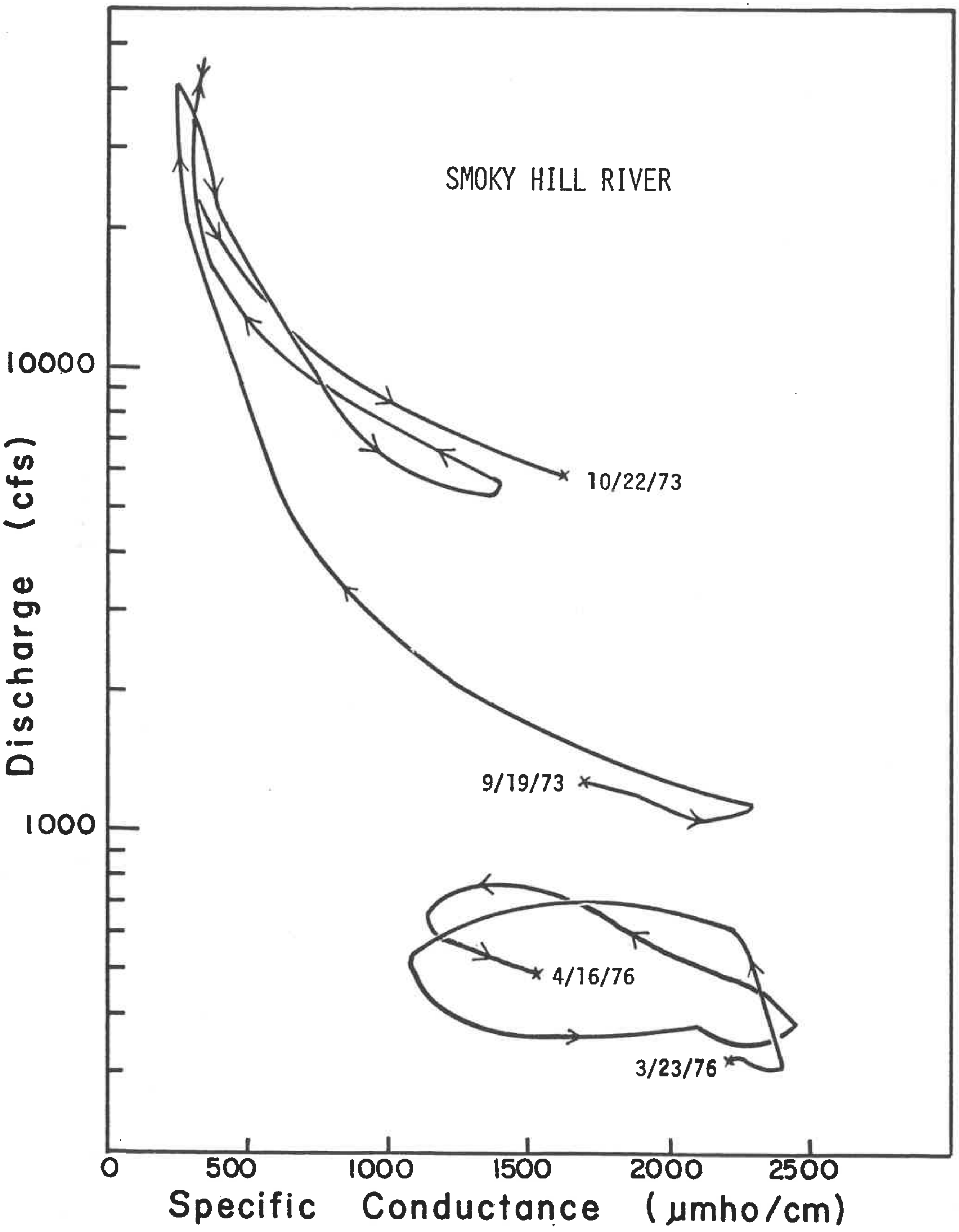


Figure 7. Discharge Versus Specific Conductance for Different Hydrologic Events of the Smoky Hill River at Enterprise.

A dilution-groundwater discharge cycle occurred in the Smoky Hill River at very large flows during the fall of 1973 (Figure 7). A period of heavy, extended rains resulted in great amounts of quickflow which rapidly flushed and diluted the water in the river, such that the flushing effect was overwhelmed by the dilution capacity of the quickflow. Specific conductance dropped rapidly at first, then at a slower rate until peak flow was reached. Great groundwater recharge occurred during this time, both from surface infiltration and seepage from the river into the alluvial aquifer, especially during flooding. As the river level dropped, specific conductance increased at a faster rate than the decrease during rising stage. The great amount of groundwater recharge either forced out large amounts of saline water derived from halite dissolution, or mixed with the saline groundwater then discharged to the river. With time, the river flow continued to fall while the specific conductance increased to complete the clockwise loop.

Variations in Na/(Na + Ca) follow cycles similar to those of specific conductance when plotted versus discharge (Figure 8). Sufficient analyses of Na and Ca do not exist in the U. S. Geological Survey records to draw the smaller cycles. However, Na/(Na + Ca) were estimated from Cl/specific conductance using previous complete analyses and the daily Cl and specific conductance records existing for the period of interest. At the start of the counterclockwise flushing-dilution cycles at lower flows during the spring of 1976, Na/(Na + Ca) first increased with rising flow as mineralized waters were flushed from the river channel and more soluble Na salts were dissolved from soils and river banks at a higher rate than Ca. The Na/(Na + Ca) then decreased with rising then initial stages of falling flow due to the lower Na/(Na + Ca) of more dilute quickflow. With falling discharge, saline groundwater inflow again became the predominant influence on the chemistry. A clockwise, dilution-groundwater discharge cycle is shown in Figure 8 for a very high flow period of the Smoky Hill River during 1973. In the first part of the cycle the chemistry of dilute quickflow is predominant, resulting in low Na/(Na + Ca) values. The point for another, even higher flow on September 9, 1973, indicates how low the ratio can drop. As more saline groundwater discharges became important with falling river flow, the Na/(Na + Ca) increased. The side protrusion in the middle of the right hand portion of the loop is due to large, saline flows released from reservoirs upstream.

As a part of this study daily samples were collected from the Smoky Hill River at Enterprise to determine the detailed changes in various major dissolved constituents with different peak discharge events: a period of snow melt, early spring rains, and thundershowers. Discharge was plotted versus specific conductance to show the types of variations occurring during these events (Figure 9). The first event, snowmelt, appears as part of a dilution-groundwater discharge cycle proceeding in a clockwise direction. The snowmelt peak existed for a few days allowing time for groundwater recharge to the alluvium, which then discharged to the river during falling stage, but contained higher TDS than quickflow. The early spring rains soon following the snowmelt did not follow any

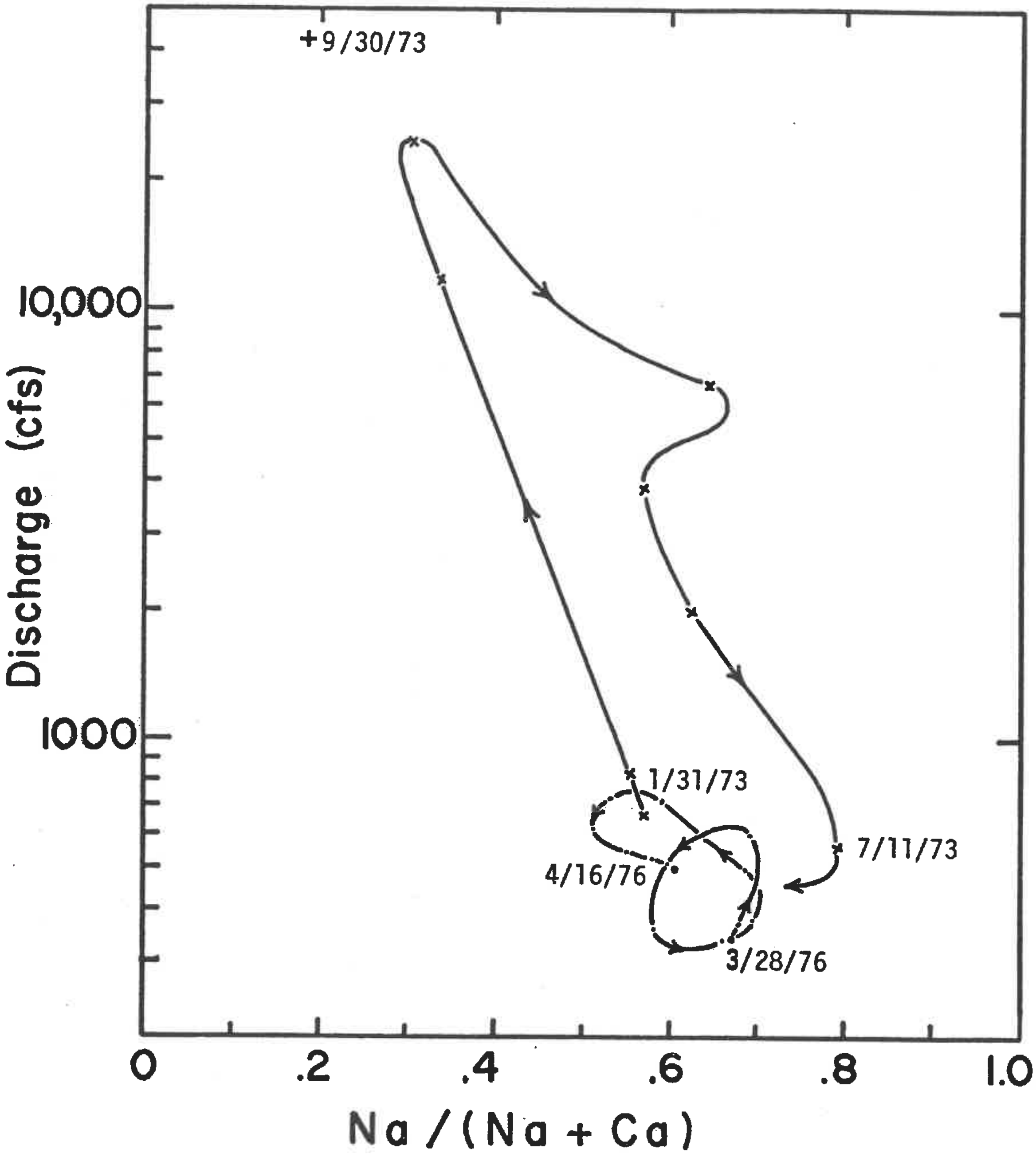


Figure 8. Discharge Versus Na/(Na + Ca) for Different Hydrologic Events of the Smoky Hill River at Enterprise.

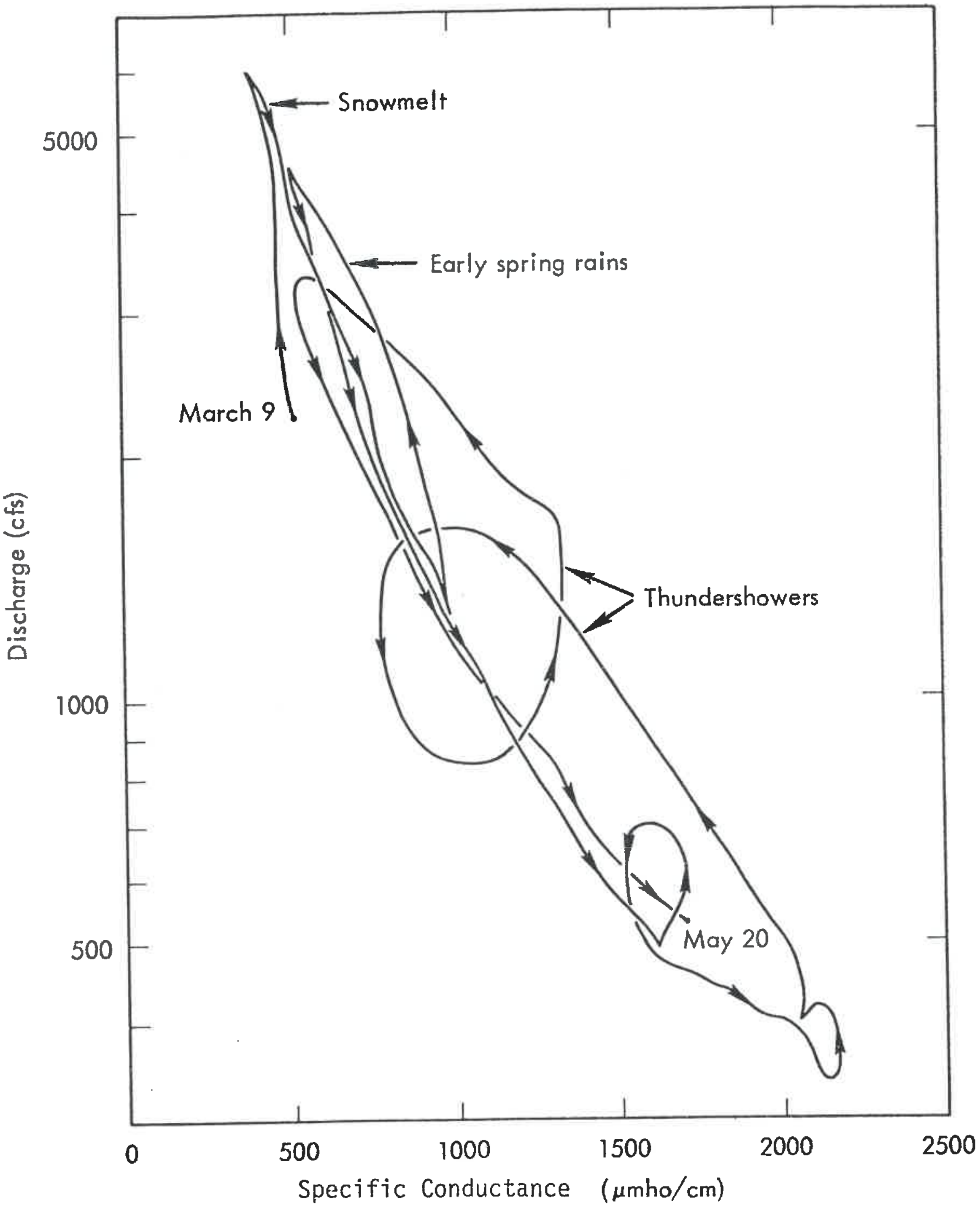


Figure 9. Discharge Versus Specific Conductance for the Smoky Hill River at Enterprise During Spring, 1978. The smallest details have been removed to simplify the diagram.

definite cycle, but rather rose and fell along the same curve. Soils had not had time to accumulate salts by evapotranspiration, and the stage of streams and the river had not dropped low enough for the channel waters to be mainly more mineralized groundwater. Thus, no flushing effect was observed. Both the snowmelt and early spring rains were fairly low in TDS in comparison with other high discharge events in other years. Also, there was apparently not enough groundwater recharge to markedly increase TDS in baseflow as following previous, larger peak flow events. Discharges from later spring thunderstorms followed definite counterclockwise loops, illustrating the flushing-dilution cycle. Here the flows had dropped low enough before the showers to allow more mineralized water to be present in the tributary and main channels, and the weather had been dry enough to allow evapotranspiration to concentrate soil moisture, such that flushing by the rains resulted in higher specific conductances than for the river recession.

A plot of discharge versus Na/(Na + Ca) is shown in Figure 10 for this same period, and is similar to a graph of discharge versus Cl/(Cl + SO_4). The variations during the snowmelt period were complex in that they indicated both clockwise and counterclockwise parts of cycles. Part of the complexity may have been due to the fact that a much larger proportion of the quickflow was initially overland flow than at other times of the year as a result of frozen soils. Flushing of salts in newly thawed, near surface, soil solutions, which may have been slowly concentrated during the dry, late fall before freezing through the record cold winter, may explain the higher Na/(Na + Ca) than expected. The early spring rains gave the lowest Na/(Na + Ca) and Cl/(Cl + SO_4) and displayed a narrow counter clockwise loop indicating that flushing of soil solutions after the snowmelt and soil thaw period was still continuing. Then, except for occasional, scattered showers which caused only minor fluctuations in the river, the discharge generally fell for over five weeks, giving time for concentration of soil solutions and inflow of more mineralized baseflow. Thus, when the larger, widespread showers occurred in early May, definite counterclockwise, flushing-dilution loops appeared for both Na/(Na + Ca) and Cl/(Cl + SO_4), especially in the first major peak flow period.

Cyclic variations in river water chemistry were discovered for other river stations studied in this research. Most of the rivers had counterclockwise, flushing-dilution cycles during discharge events. The Arkansas River at Hutchinson had narrow, clockwise, dilution-groundwater discharge cycles for very high flow events, and flushing-dilution loops for lower discharge incidents. Generalized examples of the two types of cycles are given in Figures 11 and 12 for the Saline River near Russell and Smoky Hill River at Enterprise, respectively. For the Saline River, all ranges of peak discharges investigated indicated flushing-dilution cycles, both in specific conductance and Na/(Na + Ca). Peak flow events in the lower to moderate discharge range for the Smoky Hill River also gave flushing-dilution loops. The dilution-groundwater discharge cycles only occurred for the highest peak flow incidents. Apparently, for the latter cycle to occur, a river must have good hydrologic connection to a large alluvial aquifer containing highly mineralized water, and there

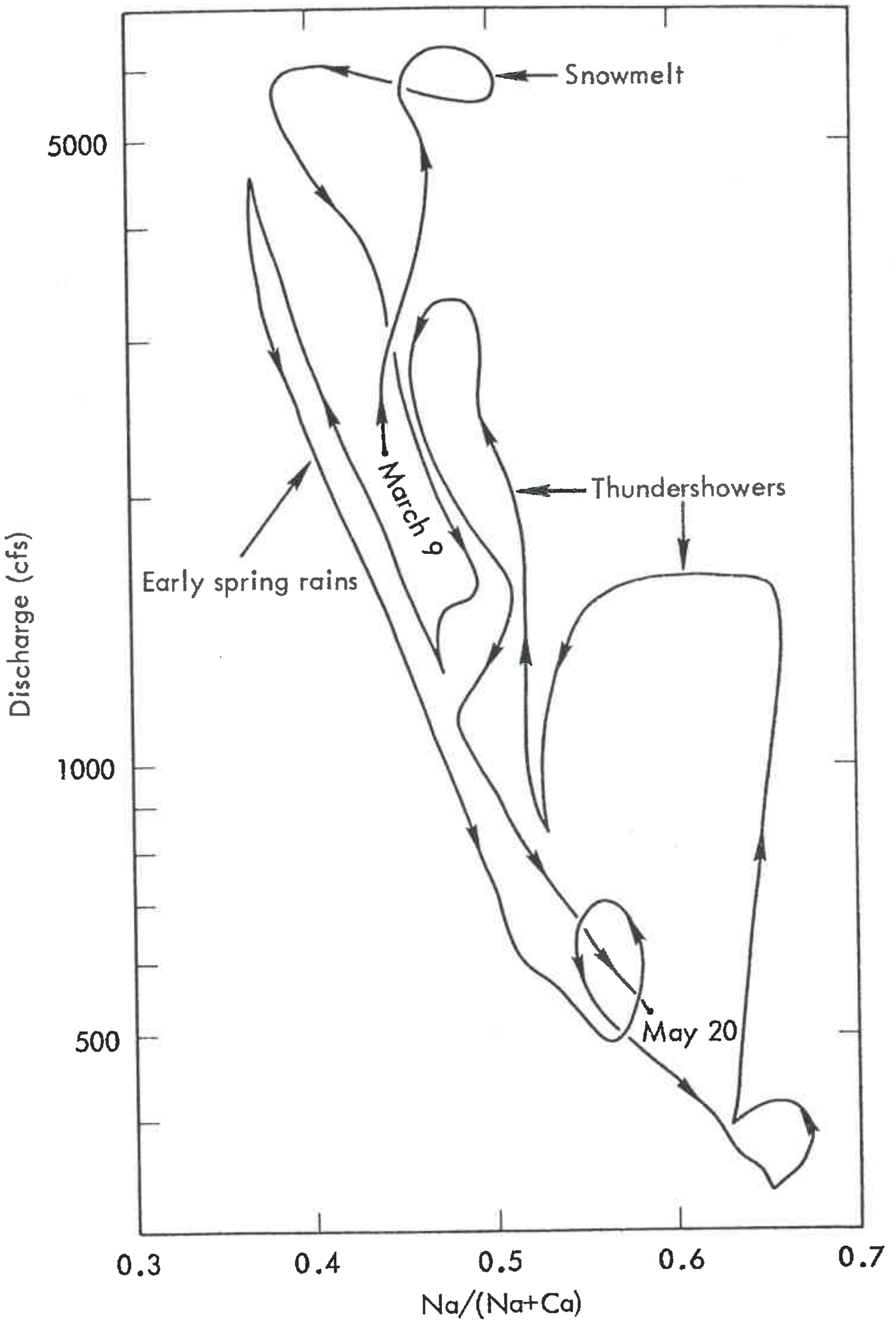


Figure 10. Discharge Versus Na/(Na + Ca) for the Smoky Hill River at Enterprise During Spring, 1978. The smallest details have been removed to simplify the diagram.

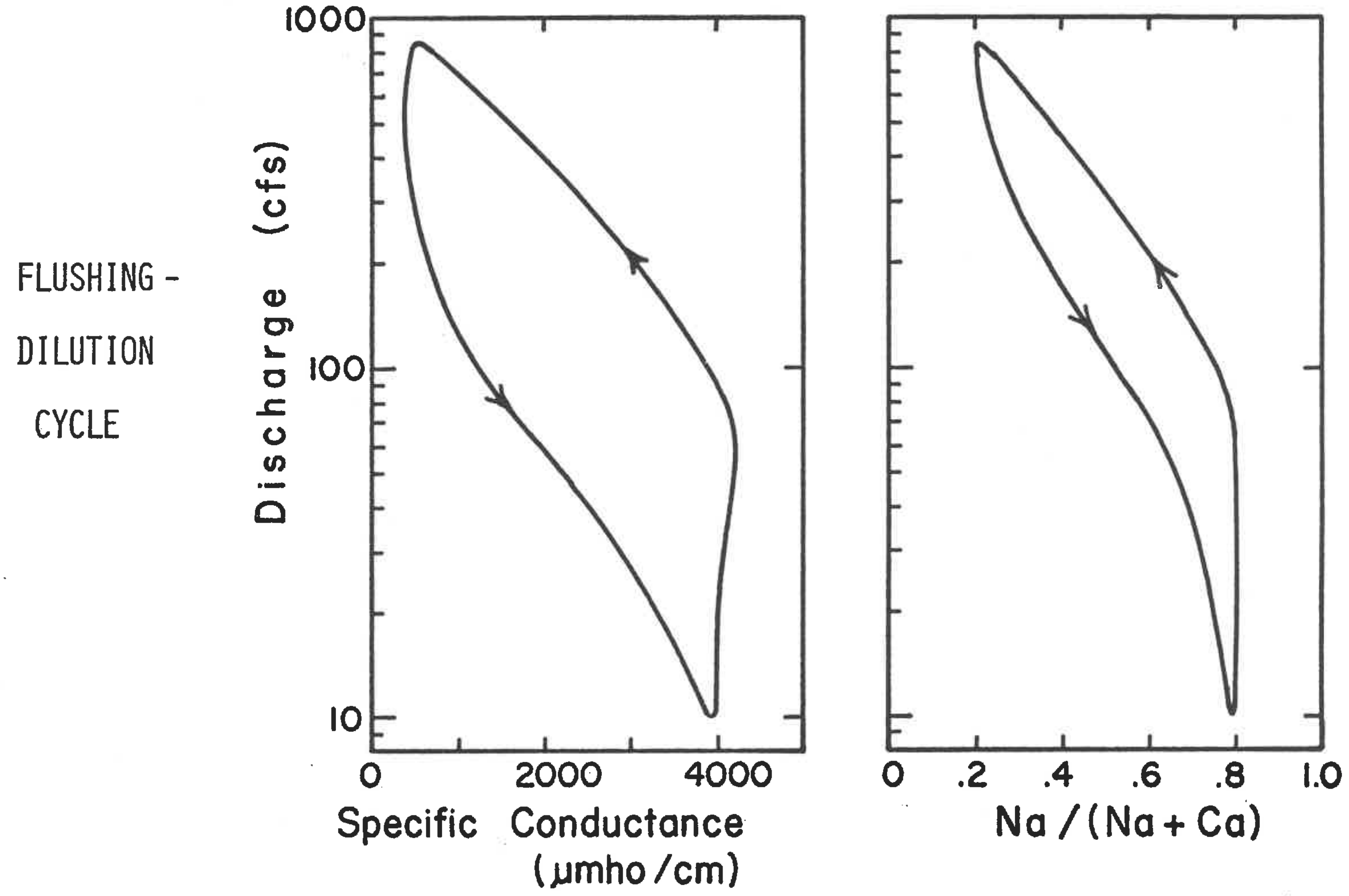


Figure 11. Generalized Cyclic Relationships of Discharge Versus Specific Conductance and Na/(Na + Ca) for the Saline River near Russell.

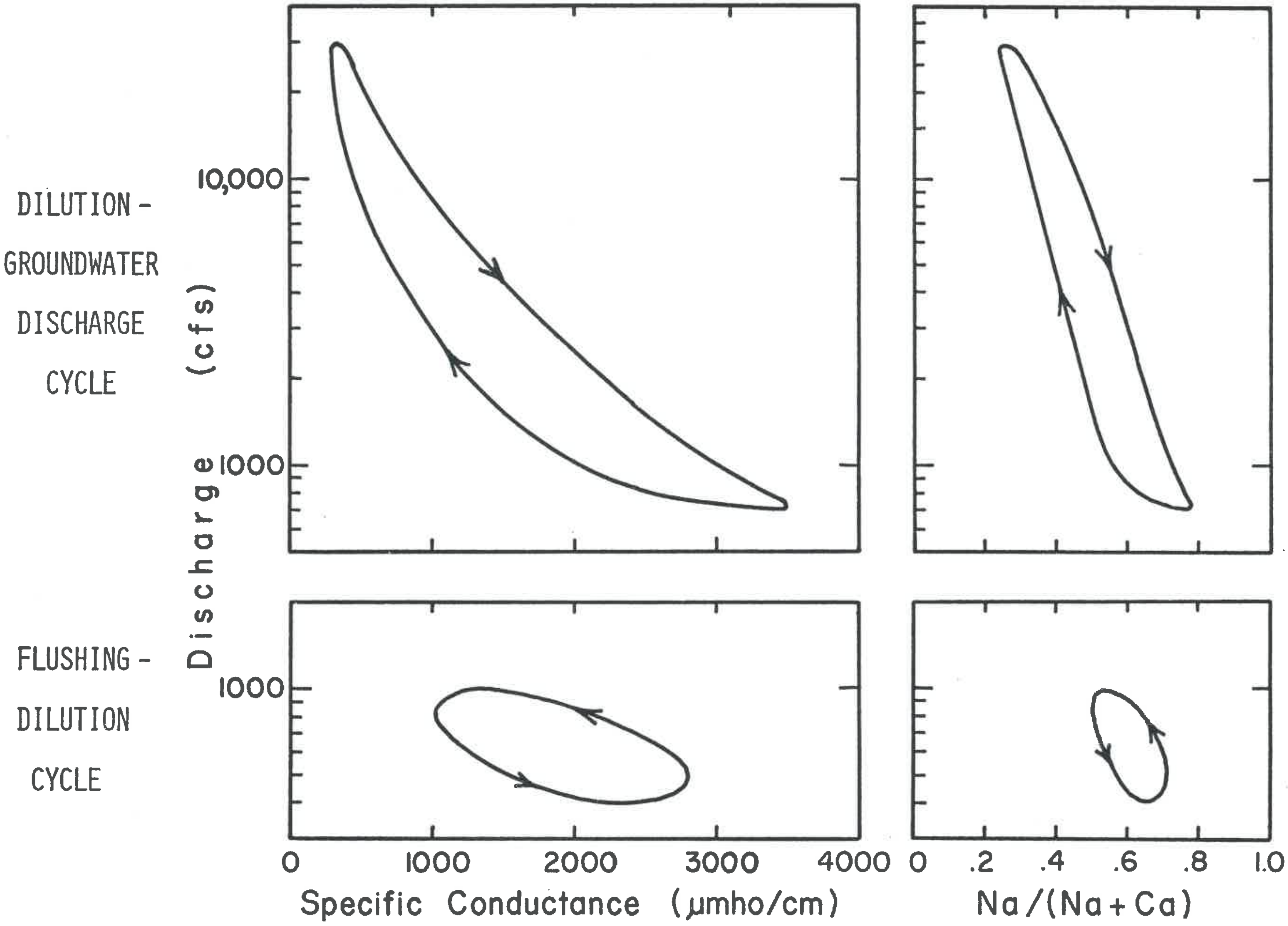


Figure 12. Generalized Cyclic Relationships of Discharge Versus Specific Conductance and Na/(Na + Ca) for the Smoky Hill River at Enterprise.

must be great groundwater recharge which causes later discharge of large amounts of the saline water. At moderately high flows compensation among the effects of flushing, dilution, and groundwater discharge produces retraced curves or narrow loops, as in the snowmelt and early spring rain events of Figures 9 and 10.

An important result of great amounts of groundwater recharge in the Smoky Hill River valley is illustrated in Figure 13. After the very heavy rains of the fall of 1973, baseflows contained very high TDS. At given discharges in the river, the TDS concentrations did not fall to usual values until over a year later. Concentrations of dissolved constituents continued to fall for given baseflows during the dry period of 1975 and early 1976. Thus, the quality of baseflows from this station and downstream are highly dependent on the previous precipitation history in the basin.

Applications to River Water Use

The great chemical variations of rivers in Kansas result in waters not meeting recommended quality standards during many periods. Recent water quality criteria include recommendations that the following major dissolved constituents not exceed certain concentration limits: Cl - 250 mg/l and SO_4 - 250 mg/l for drinking waters; TDS - 3000 mg/l for livestock (National Academy of Sciences and National Academy of Engineering, 1973). Minimum flows in Rattlesnake Creek near Raymond, the Saline River near Russell, and the Arkansas River near Coolidge are often too saline than recommended for livestock use. Low flows frequently surpass the recommended SO_4 and Cl concentrations for drinking waters in the Saline River near Russell, Smoky Hill River at Enterprise, Rattlesnake Creek near Raymond (Cl limit always exceeded), and the Arkansas River near Hutchinson and Arkansas City; the recommended Cl level is often exceeded in the Solomon River at Niles, while the SO_4 standard is surpassed frequently in the Arkansas River from Coolidge to Great Bend and occasionally in the South Fork of the Solomon at Osborne. In general, the higher the Cl or SO_4 concentrations of the lowest flows (Tables 4 and 5), the greater the period of time the river exceeds the recommended limits for drinking waters.

Although salinity and sodium hazards of irrigation waters depend on particular soils and crops, the diagram of the U. S. Salinity Laboratory (1954) generally indicates when waters could produce problems (Figure 14). The sodium adsorption ratio (SAR) - specific conductance relationships for four of the river stations studied with high TDS are plotted in Figure 14. The other river sites generally plot within the zone bracketed by the upper and lower curves, except for Rattlesnake Creek, for which the curve lies slightly to the left of that for the Arkansas River near Hutchinson at specific conductances greater than 2250 µmhos/cm, and the South Fork of the Solomon at Osborne, which lies slightly below the line for the Arkansas River near Coolidge and Dodge City at specific conductances less than 1800 µmhos/cm. The trends of the curves show that as the specific conductance and, thus, TDS of river

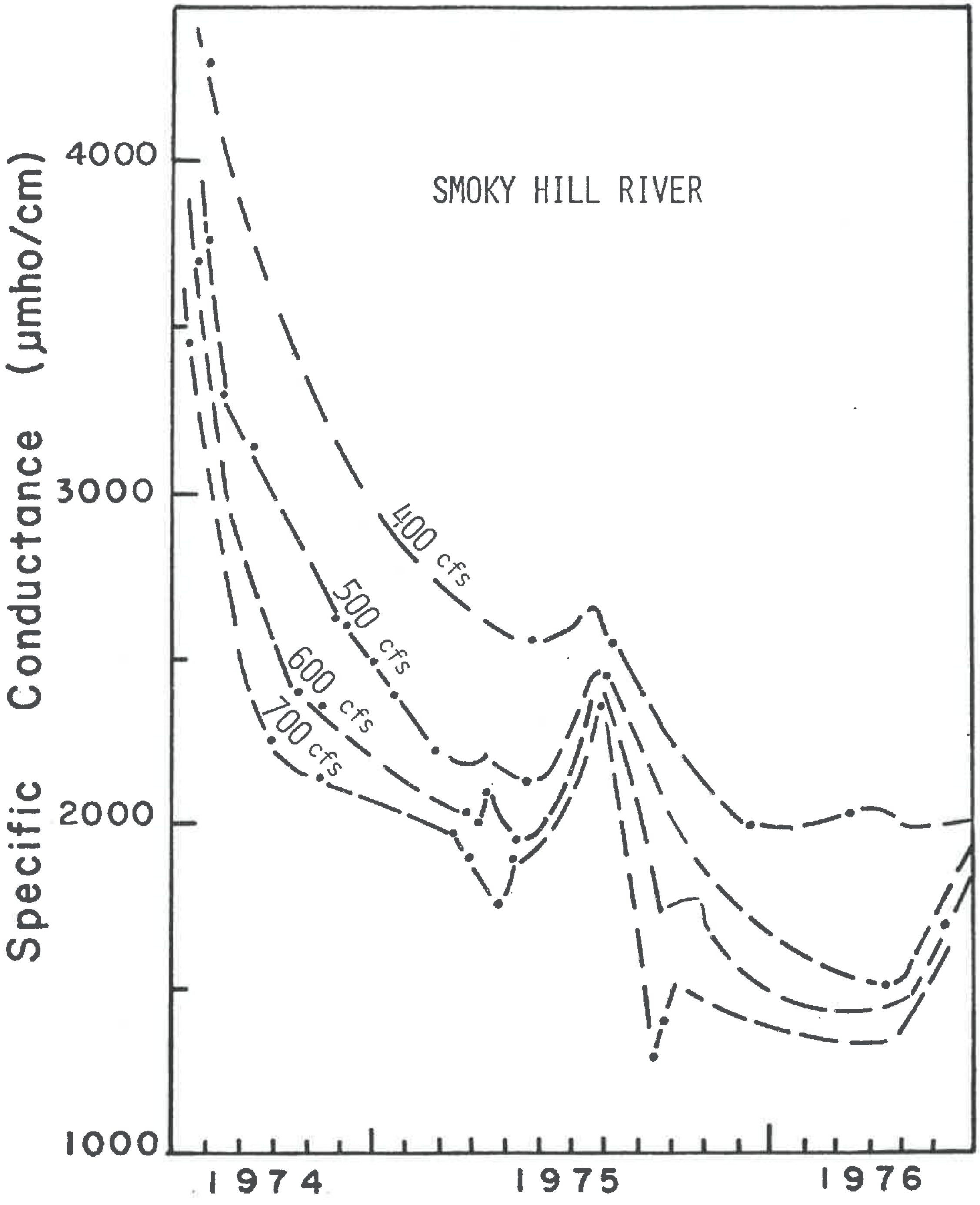


Figure 13. Specific Conductance Versus Time for Given Discharges in the Smoky Hill River at Enterprise, 1974-1976. Numbers within the graph are for discharges. Points represent observations and dashed lines indicate what the specific conductance would have been between observations if that discharge had occurred.

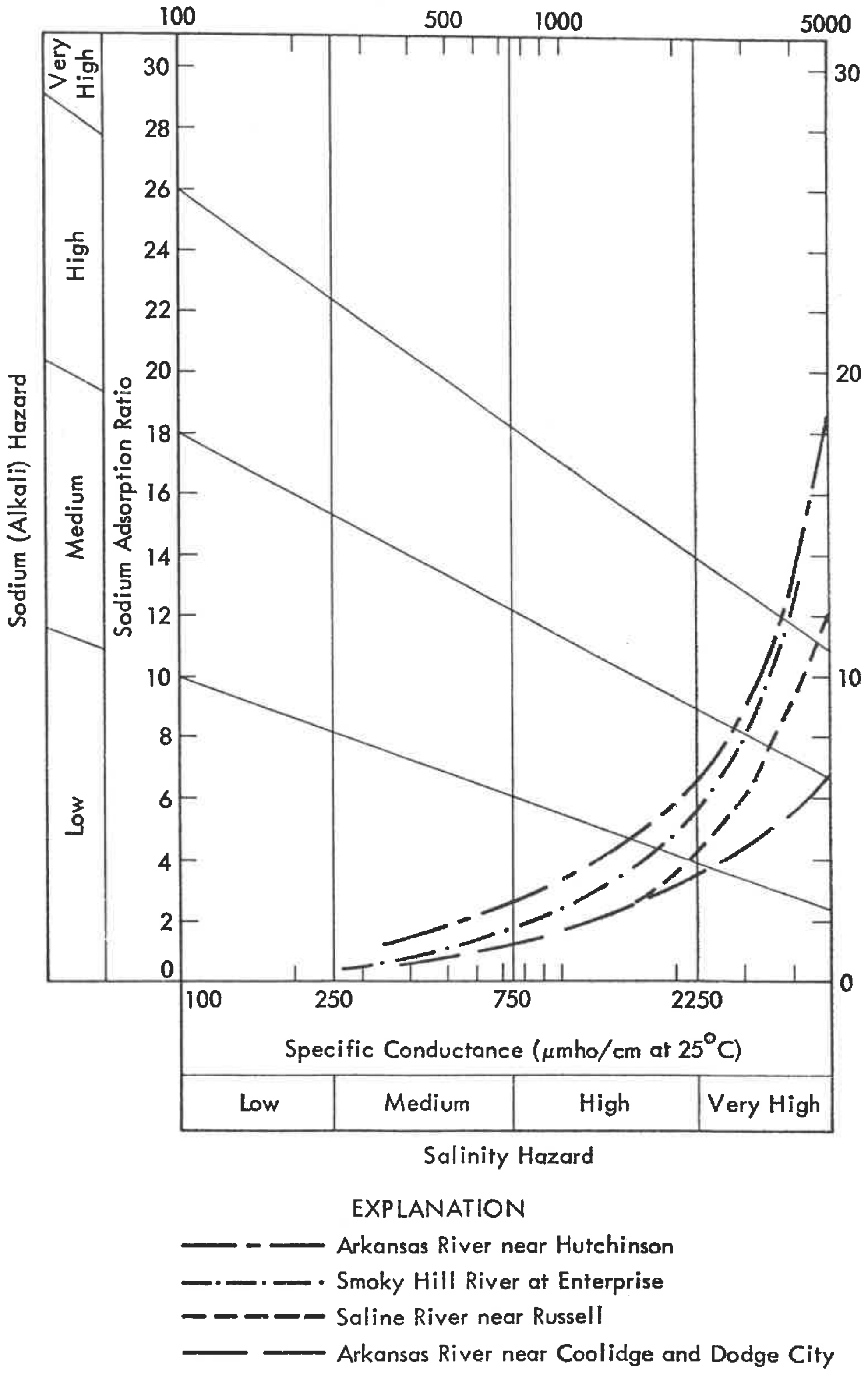


Figure 14. Sodium Adsorption Ratio Versus Specific Conductance with Irrigation Water Use Classification for Rivers in Kansas.

waters increases, the sodium hazard also increases. At high flows and low TDS the SAR increases at a slower rate with increasing TDS, than at low flows and high TDS. Rivers with saline inputs from formation waters or halite dissolution have higher SAR which increase at a greater rate with specific conductance at high specific conductances, than rivers with substantial inflows of waters from gypsum dissolution as their major mineralized source. Salinity hazards are high to very high for many of the rivers most of the time, while sodium hazards do not become high until specific conductances exceed 3000 - 4000 μmhos/cm for the saline rivers in the Kansas River basin and the Arkansas River basin from Rattlesnake Creek downstream. The sodium hazard is almost never high in the Arkansas River from Coolidge to Great Bend.

Knowledge of the cyclic variations in river chemistry, as discussed in the previous section, could be very useful in predicting when the quality of river waters will be suitable for certain uses. Within low to moderate flow ranges in all rivers studied, and also at higher flows for some of the rivers, flushing-dilution cycles occur for precipitation events. Because the water during the first part of the rise in discharge has high TDS and Na/(Na + Ca), it should not be used if possible. The best quality water occurs during the early recession phase of the hydrograph peak for small storms, and from peak discharges through the first half of the hydrograph recession for larger storms. These would be optimum times to tap irrigation waters from rivers by way of canals and ditches; the flushing part of cycles should be avoided. Flushing-dilution cycles would also be expected to occur in small or intermittent streams. Artificial recharge of aquifers by waters collected behind floodwater retarding structures on streams has been proposed for western Kansas (Gillespie and Slagle, 1972). Low baseflows and flushing discharges of poor quality should be allowed to pass through appropriately designed dams. The quality of water in larger reservoirs could also be improved by systems designed to bypass the flushing waters and minimum baseflows.

The long term changes in low flow chemistry occurring in the Smoky Hill River from 1974 to 1975 (Figure 13) can now be predicted. Water quality could be expected to decrease greatly after very large precipitation events which cause great recharge to alluvial aquifers, forcing out saline groundwater. As more data becomes available for such river sites as this, it may be possible to determine the relationship of these effects to even longer term influences of 20 year drought and wet cycles.

CONCLUSIONS

The most important factor controlling the quality of river waters in Kansas is the variation in the amounts and chemistry of quickflow versus baseflows. Quickflows (the sum of channel precipitation, overland flow, channel flow, and rapid interflow) in all rivers in Kansas are generally much lower in total dissolved solids (TDS) concentrations than baseflows. The chemistry of quickflows is controlled mainly by the removal of dissolved constituents from soils and near surface alluvial sediments, and to a smaller degree by varying amounts of dilution by direct precipitation on the water surface of river channels. The maximum dilution effect of direct precipitation is not expected to be greater than 50 percent under optimum conditions; most of the time direct rainfall would probably dilute most rivers in Kansas by less than 10 percent. In general, the farther east the river site, the lower the TDS, reflecting the increasing precipitation and decreasing evaporation rates proceeding from western to eastern Kansas. In rivers in the Kansas River watershed TDS range from 100 to 350 mg/l for very high flows; in the Arkansas River basin they extend (except for Rattlesnake Creek), from 150 to 900 mg/l.

Quickflows at all river stations studied have weight ratios of Na/(Na + Ca) which are lower, and Cl/(Cl + SO_4) which can be less than, equal to, or more than those in baseflows. In the Kansas River basin stations and the Neosho River at Parsons, Na/(Na + Ca) for very large quickflows are 0.20 ±0.05, while Cl/(Cl + SO_4) are higher and vary more (0.3 ±0.1). Higher values of Na/(Na + Ca) (0.38 - 0.25) and very low Cl/(Cl + SO_4) (0.06 - 0.17) in quickflows of the Arkansas River from Coolidge to Great Bend are partially derived from diluted baseflows at the beginning of storms, and partly from leaching of salts concentrated by evapotranspiration of irrigation and river waters in soils and near surface sediments of the broad alluvial valley. The high Na/(Na + Ca) and Cl/(Cl + SO_4) for quickflows in Rattlesnake Creek and the Arkansas River downstream of the junction with the tributary, represent salts flushed out of salt marshes and alluvial sediments.

Baseflows during dry periods in Kansas consist almost entirely of groundwater flow except at river stations where reservoir outflows provide an appreciable contribution to flow. The two main factors controlling the chemistry of ground waters are the geology and the climate. Groundwaters with the greatest TDS either have dissolved evaporite minerals (halite, gypsum, anhydrite) or are near surface, saline formation waters. Most groundwaters in Kansas are in contact with various amounts of carbonate minerals and, thus, are at least hard and Ca, Mg, HCO_3 in nature. Given areas of similar bedrock containing either evaporite minerals or saline formation waters, the greater the average annual precipitation, generally the lower the TDS in shallow groundwater.

Low baseflows greatly affected by saline formation waters (Saline River near Russell) and halite dissolution (Rattlesnake Creek near Raymond) have TDS, Na/(Na + Ca), and Cl/(Cl + SO_4) usually higher than 10,000 mg/l, 0.9, and 0.7, respectively. Minimum baseflows in the Arkansas River from Coolidge to Great Bend are controlled largely by solution of sulfate evaporites in eastern Colorado and have Na/(Na + Ca) and Cl/(Cl + SO_4) normally 0.5 - 0.6 and <0.1, respectively. Lowest flows in the Solomon River at Niles, Smoky Hill River at Enterprise, and Arkansas River from Hutchinson downstream are derived from a mixture of mineralized groundwater sources, and have TDS at least above 1200 mg/l and Na/(Na + Ca) and Cl/(Cl + SO_4) usually ranging from 0.7 to 0.9 and 0.5 to 0.8, respectively. Minimum flows in the largest river in southeastern Kansas, the Neosho River near Parsons, have TDS which seldom exceed 420 mg/l and Na/(Na + Ca) and Cl/(Cl + SO_4) which average about 0.23 and 0.33, respectively, indicating the effect of the relatively high average annual precipitation.

Evaporation of water from the surfaces of a shallow river (<0.5 ft depth) and its tributaries could possibly concentrate baseflows as much as a factor of two (50 percent reduction in original baseflow) during dry periods in the summer. The greater the depth of the river and the lower the evaporation rate (cooler and more humid seasons or more easterly location in Kansas), the smaller the effect of evaporation. Because baseflows in Kansas are probably supersaturated with respect to calcite, crystallization of this mineral during periods when evaporative concentration is greatest could noticeably increase Na/(Na + Ca) in rivers in western Kansas. The ratio Cl/(Cl + SO_4) can be used in many cases to determine whether a difference between soil moisture and groundwater chemistry or the evaporation-crystallization process is more important in controlling the change in Na/(Na + Ca) from quickflow to baseflow. The river studied which showed increasing Na/(Na + Ca) with decreasing discharge, but little or no change in Cl/(Cl + SO_4), and thus for which the evaporation-crystallization process could be important, is the Arkansas River from Coolidge to Great Bend.

Two types of cyclic relationships between discharge and water chemistry have been observed in rivers of Kansas. A flushing-dilution cycle follows a counterclockwise loop and a dilution-groundwater discharge cycle a clockwise loop when discharge is plotted versus specific conductance, TDS, or Na/(Na + Ca). The flushing-dilution cycle is found for most all peak discharge events in smaller rivers and at low to moderate discharge ranges for larger rivers. Replacement of the water in the river channel, producing a lag effect, and flushing of very soluble salts accumulated by evapotranspiration in soils and unsaturated alluvium occurs during the first part of a rainstorm. The TDS and Na/(Na + Ca) then decrease as more dilute quickflow reaches the river station and continue to decrease after the peak discharge. Then, TDS and Na/(Na + Ca) increase as groundwater inflow again becomes more important. The dilution-groundwater discharge cycle occurs for very large flows in rivers with good hydraulic connection to an alluvial aquifer containing or receiving highly saline water. Great amounts of quickflow from heavy, extended rains rapidly flush and dilute the water in the rivers, such that the flushing effect is overwhelmed by the dilution capacity and lower Na/(Na + Ca) of most of the quickflow. The TDS and Na/(Na + Ca) continue to drop until peak flow is reached. Considerable groundwater recharge occurring from the very high flow and infiltration of precipitation forces out the saline, high Na/(Na + Ca) water during recession of the river. The river flow continues to fall while the TDS and Na/(Na + Ca) increase to complete the loop. Very large groundwater recharge upstream of the Smoky Hill River at Enterprise can cause higher than usual TDS concentrations for given discharges at that station for over a year after the recharge event.

The sizeable chemical variation of rivers in Kansas result in waters not meeting recommended quality standards during many periods. Recommended drinking water limits for Cl and SO_4 are often exceeded in the Kansas River basin in central Kansas and the Arkansas River downstream of its junction with Rattlesnake Creek. Salinity hazards for irrigation are high to very high for rivers containing mineralized waters in Kansas most of the time, while sodium hazards do not become high until specific conductances exceed 3000-4000 μmho/cm for the saline rivers in the Kansas River basin and the Arkansas River from Rattlesnake Creek downstream. The sodium hazard is almost never high in the Arkansas River from Coolidge to Great Bend.

The relative contributions of the different natural factors controlling inputs of major constituents as determined in this study can be applied to improving models of river water quality used for predicting future variations or separating the effects of anthropogenic sources of pollution. Knowledge of the cydic variations occurring in river water chemistry can improve the determination of the type and period of high discharge events in which the water quality of rivers normally high in dissolved solids would meet standards for drinking and irrigation use.

RECOMMENDATIONS

Recommended Procedures for Water Use and Quality Control

1. Avoidance of River Water Use During the Flushing Parts of Cyclic Variations in Quality--Water flowing during the first part of a rise in discharge in rivers in western and central Kansas following a dry period of more than a week have high TDS and Na/(Na + Ca) as a result of flushing, especially in the warmer months when evapotranspiration is high. If the river water quality before the rain or snowmelt is close to or does not meet the recommended levels of major dissolved constituents for drinking or irrigation use, any withdrawals from alternate sources of supply should be continued until after the flushing period. Also, floodwater retarding structures collecting waters for artificial recharge of aquifers should be designed to allow the passage of flushing and low baseflow discharges. This would prevent saline pollution of the aquifer.

2. Control of River Water Quality by Flood Retarding and Recharge Structures Upstream of Mineralized Groundwater Inflows--Seven different procedures have been suggested for the elimination or reduction of natural brine flows reaching streams in Kansas (Kansas Water Resources Board, 1977). An additional procedure which has advantages over the others has been formulated as a result of this study. The method involves modification of the artificial recharge project proposed by Gillespie and Slagle (1972). A system of flood retarding structures and low-head dams should be built far enough upstream of saline inflow areas, that recharge increases good quality baseflow, but does not provide recharge to move out additional saline groundwater. The principal modifications are the appreciable enlargement of the outlet drains and the placement of low-head dams on small perenial, as well as emphemeral streams. A series of retarding structures would be built in small watersheds near the heads of tributaries. The low-head dams would be constructed in tributary stream channels such that very high waters could pass without flooding adjacent fields substantially more than would have occurred without the dams. Large outlet drains should be placed at the base of the structures and dams to allow sediment to be carried through. A design emptying time of the drains of two to three days for 80 percent of the detention capacity and four to six days to

empty should be large enough to permit much of the mineralized flushing quickflow and all of the baseflow in perennial streams to pass without retention, thus allowing only high quality water to recharge aquifers. The function of the system is to increase groundwater recharge to freshwater aquifers, thereby increasing the quantity of good quality baseflow, and to decrease flood flows in the areas of saline discharges, thus diminishing the amount of recharge to the mineralized groundwater and salt deposits. The plan has the advntage of not only increasing the amounts of fresh baseflow that dilute mineralized low flows downstream, but also decreasing the quantities of saline baseflows. In addition, groundwater resources would be replenished. Although recharge would not be as great as in the project proposed by Gillespie and Slagle, the larger drains would have the advantage of allowing no appreciable sediment deposition and would clog much less than the smaller outlets. The method suggested here should be better than larger reservoirs in western and central Kansas which fill with sediment and become more mineralized with time during dry periods due to evaporative concentration.

Recommended Future Research

1. Extension of Study to All River Water Quality Stations in Kansas--The procedures used in this study should be applied to all of the river water quality stations in Kansas. A map outlining areas of different chemical controls should be prepared for use in water resources management and planning.

2. Application of Results to River Water Quality Models--The results of this study should be incorporated in existing computer models of water quality to greatly improve their resolution of the variations in chemistry with discharge. This will be necessary before most nonpoint and some point sources of anthropogenic pollution can be distinguished from the natural variations of many rivers in Kansas. The model could also be used to show long term quality changes caused by man as additional records become available, and to predict changes produced by precipitation events and droughts.

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