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**EXTRACTION OF INFORMATION  
ON  
INORGANIC WATER QUALITY**

by  
**William L. Lane**



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COLORADO STATE UNIVERSITY  
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The research work leading to this paper was supported by National Science Foundation Grant GK-31512 on the project "Stochastic Processes in Water Resources," in the Hydrology and Water Resources Program of the Department of Civil Engineering at Colorado State University, Fort Collins, Colorado, Colorado State University Experiment Station.

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## ACKNOWLEDGEMENTS

I wish to express appreciation to my major professor, Dr. Vujica Yevjevich, for the guidance and helpful suggestions given during the course of Ph.D. studies and the preparation of this paper. As academic advisor, Dr. Yevjevich has made a beneficial contribution throughout my studies at Colorado State University. Thanks are also extended to Dr. Janet G. Osteryoung who generously gave of her time providing valuable advice and guidance during much of this study and who contributed greatly to improving the preliminary draft. I acknowledge with gratitude the advice and suggestions of the other individuals who helped such as the members of my Ph.D. committee: Dr. Duane C. Boes, Dr. David W. Hendricks, Dr. M. Moinuddin Siddiqui, and Dr. Daryl B. Simons. Special thanks are also due Dr. Thomas G. Sanders who took time to carefully read the first draft and to make suggestions. Dr. Sanders' advice, suggestions, and insight were particularly valuable.

Appreciations go also to fellow graduate students, particularly Dr. Leonard J. Lane, who provided constructive criticism during the study and by carefully reading the preliminary draft.

Financial support for this study was received from Colorado State University Experiment Station and from Research Grant GK-31512, "Stochastic Processes in Water Resources," of the National Science Foundation, with Dr. Yevjevich as principal investigator. This support is greatly appreciated.

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## ABSTRACT

The potential for obtaining information concerning certain water quality variables on a stream by considering the relationships which exist between quality and quantity variables is examined. More precisely, the study is concerned with the relationship which exists between discharge and inorganic water quality in natural streams. Inorganic water quality is taken to refer to the concentrations of inorganic constituents found dissolved in the stream water. Natural streams are defined as those streams which are free of man's influence, although some compromise of this definition is necessary in actual application. The relationship studied is the negative correlation between inorganic water quality and discharge which is found in virtually all streams. Study is limited to thirteen inorganic constituents: silica ( $\text{SiO}_2$ ), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), bicarbonate ( $\text{HCO}_3$ ), sulfate ( $\text{SO}_4$ ), chloride (Cl), fluoride (F), nitrate ( $\text{NO}_3$ ), boron (B), and pH (minus the logarithm of the hydrogen ion activity). In addition, conductivity is taken as an indicator of the total inorganic dissolved solids concentration.

Applications are made using data from five streams: the Henry's Fork River at Linwood, Utah; the New Fork River near Big Piney, Wyoming; the Pecos River near Puerto de Luna, New Mexico; the Saline River near Russell, Kansas; and the Wind River at Riverton, Wyoming. The same approach is used with data from each of the five streams and similar results are noted.

The approach consists of three basic parts. The first part is to develop the relationship between conductivity and discharge. The second part is to relate the constituent proportions to discharge. The final part is to develop a relationship between the constituent concentrations and the conductivity. By using these three parts together, constituent concentrations are predicted from the stream discharge alone. The relationship between constituent concentrations and conductivity is based on chemical theory and is applicable to any stream sample. The other relationships have parameters which must be determined for each individual stream.

The procedures and mathematical models presented in this study show promise of being generally applicable to all natural streams. In addition to extracting water quality information from discharge data, there are three areas of application which are also significant. First, the methodology shows promise of improving the understanding of water quality behavior and its relationship to discharge. Second, the development of relationships of this type allows a basis for meaningful judgments to be made concerning trends or other changes in the quality of a stream. Third, the relationships developed allow the possibility of analyzing and improving water quality sampling.

## FOREWORD

In the past, sanitary engineering has been primarily concerned with water quality problems. In order to obtain a desired water quality for community and industrial supplies, it was necessary to first investigate the quality of available water and if necessary, plan measures to provide water of sufficient quality. With the continuing, undiminished demand on

water resources and the increased influence of man on water quality of all bodies of water, the importance of studying water quality processes in nature has increased significantly and subsequently is no longer the domain of only sanitary engineers. A much broader approach taking into account the hydrologic cycle is required.

The primary objective of advanced hydrology is the investigation of various water processes in nature. Particular stress on studies of these water quality processes results from their importance in water resources development, water conservation, and in environmental control. A broad understanding of interactions between water quantity and water quality variables is a prerequisite to solutions of these various economic and social problems. The modern definition of hydrology refers to distributions of water quantity and water quality variables in space and time. Thus emphasis is placed on the understanding of how water quality properties evolve from both natural and man-affected conditions in various bodies of water.

The environmental design of land use and planning and development of water resources require substantial information on water quality. Because the interaction between water quantity and water quality variables is often complex, it should be expected that water quality hydrology, both on a theoretical and on an applied level, will be a major subject for research efforts and for a generalization of information in the near future. Assuming that water quality is described by sets of physical, biological and chemical variables, which are mutually related, the problems of expressing water quality parameters in terms of water quantity variables have consistently been of interest to water resources specialists.

It is often useful to express water quality properties as a function of the water regime and relate them to various river basin factors. It is now apparent from many references that water quality hydrology and the interrelationship between water quality and water quantity variables are receiving an ever increasing importance. For several years efforts have been undertaken within the graduate and research Hydrology and Water Resources Program of the Civil Engineering Department at Colorado State University to develop research capacity oriented to water quality hydrology. The Ph.D. thesis in the form of this paper by Dr. William L. Lane is the result of these continuous efforts.

In establishing the collection procedures for hydrologic data many decades ago, the simple idea imposed by economical constraints, was to measure the water quantity variables and investigate the relationships between water quality and water quantity. When the relationships between water quality and water quantity variables are sufficiently strong, the information available on water quantity became easily transferable to water quality variables. The expectations from this simple idea resulted not to be as feasible as originally conceived. Often, the relations between water quality and quantity are weak, explaining only a small portion of the total periodic stochastic variation of water quality. Sometimes, explained variances of water quality processes by such relations did not exceed ten, twenty, or thirty percent. Taking into account that often the average values of water quality for larger time intervals were used in developing these relations, the transferred information for the short time intervals would be even less reliable.

There is a large number of variables which describe water quality. With so many chemical compounds and heavy metals dissolved in the water, and the other properties of water quality, several hundred variables can be identified that would be necessary for a comprehensive description of water quality. It is not, however, economically feasible to regularly record or observe all these hundreds of variables. Therefore, it

is necessary to establish a hierarchical system of variables with different levels of importance, having a small number of observed quality variables. By establishing sufficiently high relations between the unobserved and the observed water quality variables, a large portion of information from observed to unobserved water quality variables can be transferred.

This hydrology paper by Dr. William L. Lane is a search for strong interrelationships between the inorganic water quality characteristics and the selected general water quality variables as well as the water quantity. It should be viewed also as an effort to find a minimum number of variables, related to inorganic water quality, that should be observed. With the data resulting from the chemical analysis of a few water samples from time to time mathematical relations may be established between the unobserved water quality variables and the general water quality variables regularly observed. This would enable the improved transfer of water quality information beyond the original concepts and ideas of transferring information on water quantity to information on water quality. The progress toward achieving a better understanding of factors affecting water quality will be accomplished by including a small set of water quality variables into the regular observational network of water gauging stations.

It is logical to expect that the pressure on water resources and the increase of the importance of water quality control with time would require new approaches for procuring information on water quality variables. Two reasons favor this expected development: (1) the outpouring of waste waters and airborne pollutants into nature, and (2) the ever increasing need for information on water quality.

If the properties of all types of geophysical time series are surveyed, a general conclusion may be drawn that the more water passes through different environments, the more complex the periodic-stochastic water quality processes become. The water quality time processes are among the most complex time processes of nature. Besides, the impact by man on hydrologic environments create a continuous change in water quality variables, making their time processes both inconsistent (or subject to systematic errors) and non-homogeneous (as the man-introduced changes).

Regardless of the fact that physical and biological water properties cannot be disassociated from the inorganic chemical composition, the use of a step-by-step approach with a separate analysis of water quality properties of inorganic dissolved matter is necessary. If separate analyses of various water quality characteristics are properly made, then, the overall synthesis of all dependent water quality properties related to the water regime, and to various river basin factors, is an excellent goal and probably one of the best approaches to the transfer of knowledge of water quality variables from one river basin to another. In this transfer, the factors of geology, soil composition, vegetation, groundwater aquifers, use of land in river basins, and some other factors may help explain a large portion of variations of water quality processes.

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## Chapter 1 INTRODUCTION

### 1.1 Scope

All aspects of the character of a stream's hydrologic system may be classified under two very broad categories, quantity and quality. While hydrologists have long studied those aspects relating to quantity, the quality aspects have been neglected. This study examines the potential for obtaining information concerning certain quality variables on a stream by considering the relationships which exist between quality and quantity variables on a stream. More precisely, this study is concerned with the relationship which exists between discharge and inorganic water quality in natural streams.

Discharge is taken to be the mass rate of flow in the stream. Inorganic water quality for the purposes of this study refers to the concentrations of inorganic constituents found dissolved in the streamwater. Inorganic constituents (inorganics) are generally those constituents which do not contain carbon and may be thought of as resulting from the dissolution of inorganic (noncarbon) compounds. A number of synonyms for making reference to the concentration of inorganics in solution have developed into common usage. Since the inorganics account for virtually all of the dissolved solids found in most streams, the term total dissolved solids or simply dissolved solids is often used intending reference only to the inorganic constituents. Likewise, because the inorganic constituents may have come into solution through the dissolution of chemical salts and are predominantly in ionic forms within solution, terms such as total salt content, salt load, salt concentration, ionic concentration, and ion concentration are common. Obviously, in many cases, the use of these terms is not completely correct. In this study a few of these terms will be used. However, it should be made clear that in all cases the references are to the dissolved inorganic constituents. A more complete discussion of inorganic water quality follows in Chapter 2. Natural streams are taken to be those streams which are free of man's influence. Obviously, some compromise in regard to this must be made when selecting actual data. The data selection process is described in Chapter 4. The relationship with which this study is concerned is the well documented (see Chapter 3) negative correlation between inorganic water quality and discharge which is found in virtually all streams. Hereinafter this relationship will be referred to as the discharge-quality relationship. In exploring the discharge - quality relationship, data for both discharge and the inorganic constituents is obtained for a known point along the stream. Therefore the relationship examined is that for a given stream at a given point and is not transferable to any other point on the same stream or to any other stream. The exact form and quantity of data obtained for this study are described in Chapter 4.

Study is limited to thirteen inorganic constituents: silica ( $\text{SiO}_2$ ), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), bicarbonate ( $\text{HCO}_3$ ), sulfate ( $\text{SO}_4$ ), chloride (Cl), fluoride (F), nitrate ( $\text{NO}_3$ ), boron (B), and pH (minus the logarithm of the hydrogen ion activity; see also Chapter 2). The terminology used in reference to the thirteen constituents is that normally used by the U.S. Geological Survey (Brown et

al., 1970) and will be adhered to throughout this study. Conductivity, or more precisely specific conductance, is also studied. The conductivity, or ability of a solution to carry an electrical current, is an indirect measure of the total dissolved solids concentration in solution (Hem, 1970). It is studied in detail in later chapters and is treated as the single most important water quality variable in this study due to the approach taken.

### 1.2 Objective

The objective is to provide an improved modeling procedure for the relationship which is known to exist between stream discharge and the inorganic water quality. If the relationships between water quality and water quantity variables can be easily and accurately determined, a great deal of information on the water quality variables can be obtained from previous flow records and from a limited number of chemical analyses and other quality measurements. The most economical technology for obtaining information on water quality variables is still to be developed. A goal of this study is to provide an objective approach for establishing the discharge-quality relationships within natural streams which may aid in determining that technology. Since the discharge-quality relationship has been recognized and studied in the past (see Chapter 3), the objective clearly is to make further improvements.

There are a number of areas in which past studies may be criticized. First, there has been no agreement on or determination of the general form which the discharge-quality relationship should take. The approaches have been varied and no one approach has been found to be superior. Seldom has an investigator examined more than one type of approach. Generally, in each study only one stream has been examined. In addition, the same data usually are used for determining the parameters of the relationship and for measuring the goodness of fit of the relationship. This fitting procedure is often questionable, especially in cases where the data are limited and the number of parameters large. Studies in the past have been concerned generally with only a very few constituents, often only one constituent. The effects of seasonal variations have been handled only occasionally and then by graphical or subjective methods which are not well adaptable to general use. Most studies have been made using average monthly or annual data which tend to mask the true relationship which exists when using more frequent data. Daily variations which are often large and significant are largely unaccounted for when using widely spaced data. In addition, little use has been made of knowledge which exists in the area of aqueous chemistry.

The specific objectives of this study are aimed primarily at correcting some of the faults or weaknesses of past studies. There are ten specific objectives:

1. Provide a general approach. To accomplish this, five streams are selected for study. The selection process and the data obtained is described in



Chapter 4. The same methods will be applied to each of the five streams.

2. Objectively select the basic form for the discharge-quality relationship by considering several potential forms.

3. Develop an objective approach toward parameter estimation.

4. Study data on a daily basis in as far as the available data permits.

5. Treat the effects of seasonality (time of year) in an objective manner.

6. Examine and study the relationships existing for all of the commonly determined inorganic constituents. These thirteen constituents were named in the previous section.

7. Provide confidence in the fitted relationships by considering goodness of fit statistics for both data which were used to estimate the parameters and data which were not. This will lend confidence that the relationship which is estimated is the true relationship and not simply a reflection of the sample set used in estimating the parameters.

8. Provide a methodology which is compatible with the data generally available on streams within the United States.

9. Make efficient use of the available data in order to extract the maximum amount of information possible.

10. Make use of presently available knowledge in the area of aqueous chemistry where applicable.

One limitation has been made in selecting objectives for this study. This study is not intended to justify the full and complete use of quality data obtained via the use of the estimated relationships and discharge data in place of actual chemical analyses. This justification, if it exists, is left for later studies. It is expected that the uses intended for the quality data would greatly influence the potential acceptability of predicted rather than actual data. Although justification in this regard will not be made here, it is conceivable that it could be made. In fact, the seriousness of errors which would result from the use of estimated discharge-quality relationships could very likely be found to be no more than that involved in using infrequent grab (instantaneous) or composite samples.

### 1.3 Approach

One of the main considerations involved in selecting the basic approach is the data availability. In order to arrive at a generally applicable methodology, the approach must fall within the limitations imposed by the generally available data. Since some variation in the form and completeness of chemical analyses data is expected, the methodology must be versatile enough to accept imperfect data.

To best meet the objectives and satisfy the various data constraints, a three part approach is selected. The first part is to develop the relationship between conductivity and discharge. By selecting

conductivity as an indicator of the total inorganic concentration, several advantages are readily apparent. Most of the variations in the individual constituents are explained by the variations in the conductivity (for example see Hendrick, 1970; Ledbetter and Gloyna, 1964; or Hem, 1970). Also, conductivity data are generally on a daily basis and therefore well adapted to study, especially in regard to seasonality. Conductivity are generally the most abundant inorganic quality data available on a stream. Since the total concentration is the most important variable, conductivity is well suited for playing the role as an indicator or variable of the total concentration. As a general illustration of the time series involved, Figures 1-1 through 1-3 indicate the river flow and conductivity time series for one year on three of the streams studied. As shown in the figures, there is a strong relationship between the flow and conductivity on a stream. Periods of high flow are characterized by low values of conductivity. Conversely, periods of low flow are characterized by high values of conductivity.

Flow, cfs;  
Conductivity,  $\mu\text{U}/\text{cm}$

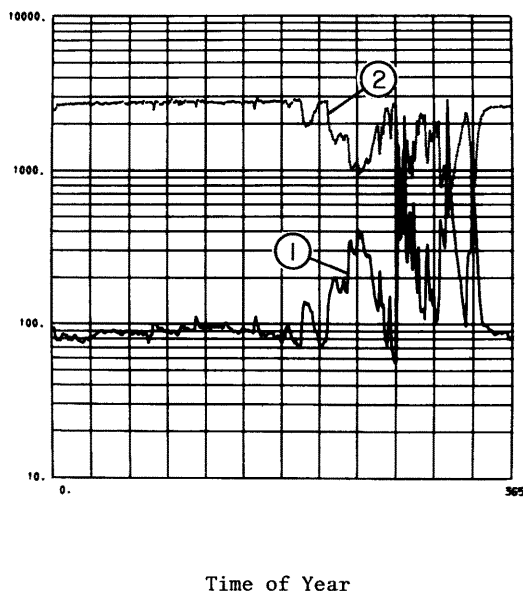


Figure 1-1. Flow (1) and conductivity (2) time series of the Pecos River for the water year beginning October 1, 1967.

The second part is to relate the constituent proportions to discharge. The proportions are relatively constant when compared with the constituent concentrations. In fact, it has been pointed out by Hem (1970) that in past studies the constituent proportions have often been taken as constants.

If conductivity was exactly the same as the total concentration, the study would be complete. Unfortunately conductivity is only an indicator of the total concentration. Therefore a relationship between

the constituent concentrations and the conductivity is determined. The relationship is based on chemical theory. The relationship is such that when given the

Flow, cfs;  
Conductivity,  $\mu\text{U}/\text{cm}$

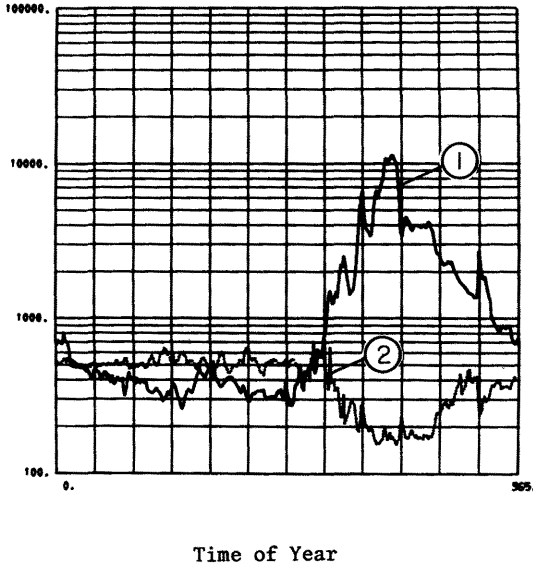


Figure 1-2. Flow (1) and conductivity (2) time series of the Wind River for the water year beginning October 1, 1965.

conductivity and the constituent proportions, it is possible to determine the constituent concentrations. Unlike the first and second relationships, this relationship is generally applicable to all streams without any parameter estimation. Simplifications to the relationship are also considered.

#### 1.4 Significance

Aside from simply improving the approaches towards relating quality to quantity in a stream, there are three areas of significance. First, an understanding of water quality behavior and its relationship to discharge is important. Second, the development of relationships of this type allows a basis for meaningful judgments to be made concerning trends or other changes in the quality of a stream. By removing the effects of discharge and time of year from the actual data, changes such as a deterioration of the water quality of a stream become more easily recognized. Third, the relationships developed allow the possibility of analyzing and improving the effectiveness of water quality sampling. Areas of possible application include studies of required sampling frequencies, value of compositing samples, and other aspects of water quality sampling techniques.

#### 1.5 Organization

The following three chapters provide further background for the rest of the study. Chapter 2 deals

with some pertinent aspects of inorganic water chemistry and is intended for those readers not familiar with this subject. Chapter 3 presents a brief discussion of the more important contributions in the area

Flow, cfs;  
Conductivity,  $\mu\text{U}/\text{cm}$

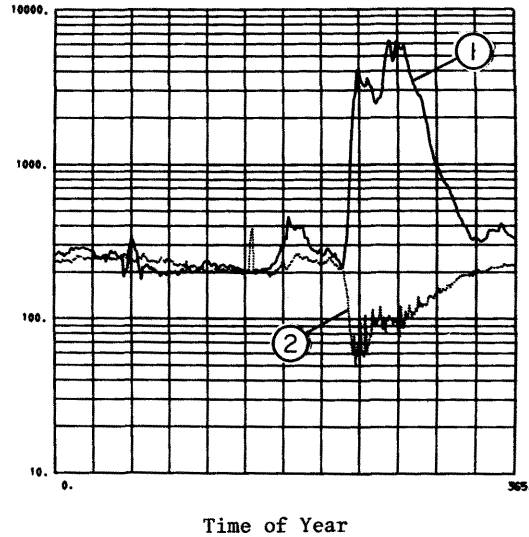


Figure 1-3. Flow (1) and conductivity (2) time series of the New Fork River for the water year beginning October 1, 1966.

of discharge-quality relationships. This discussion provides a basis from which to proceed. Some readers may not find it necessary to read this section provided they are familiar with the subject area. Chapter 4 covers the data selection process, and a description of the data selected is given. This section while necessary and of importance is primarily composed of background information.

Following the three chapters of background material, the next three chapters present the essential aspects of this study: Chapter 5, the relationship between discharge and conductivity; Chapter 6, the relationship between constituent proportions and discharge; and Chapter 7, the relationship between conductivity and constituent concentrations. Actual data from each of the five streams selected for study are used throughout these chapters. At the end of each of these three chapters is a summary of the methods used.

The mathematical methods used in the study are further clarified and explained in Chapter 8.

Chapters 9 and 10 deal with the application of the fitted relationships for the purposes of prediction and simulation of daily water quality data.

The final chapter deals with conclusions and recommendations for further study.

## Chapter 2 BACKGROUND INFORMATION

This chapter presents a brief discussion of pertinent inorganic water chemistry. While most of the information presented here is somewhat elementary, it is felt that since this work is intended primarily for use by hydrologists rather than water chemists, a discussion would be beneficial. Detailed information may be found in numerous references such as Hem (1970), Brown et al. (1970), Powell (1964) and Garrels and Christ (1965).

### 2.1 Chemical Composition of Natural Waters

Dissolved solids in natural waters may be either inorganic (containing carbon) or inorganic forms (not containing carbon). Since organic compounds are generally insoluble in water, virtually all dissolved solids in natural waters are the result of the dissolution of inorganic compounds. The inorganic dissolved solids may be in either an ionic form, that is, carrying an electrical charge, or a nonionic form. Positively and negatively charged ions are referred to as cations and anions, respectively.

The inorganic dissolved solids may be attributed to dissolved chemical salts (compounds containing metal ions and acid radical ions). As a result the dissolved solids are often referred to as dissolved salts and terms such as salt load and salt content are commonly used.

Concentrations may be expressed in a number of ways. Those used in this study are weight fraction, moles per liter and equivalents per liter. The weight fraction of a solute is the fraction of the total solution weight due to that solute and is expressed in terms of parts per million, weight percentages, or similar units. The number of moles per liter of a solute is the number of gram-molecular weights of solute per liter of solution. The equivalents per liter concentration designation may be applied to either individual ions or to salts which dissociate into ions. For an individual ion, the number of equivalents per liter is equal to the ion's number of gram-molecular weights per liter multiplied by the ion's valence. For a salt the equivalents per liter concentration is equal to the sum of the equivalents per liter concentrations of all of the resulting anions (or cations since the sum of the anions must equal the sum of the cations to satisfy an electrical charge balance).

The exact forms of many of the inorganic dissolved solids are not always known from the chemical analyses. As a result some constituents are reported in terms of concentrations of elements or compounds while others are reported in terms of ions or ion radicals. For example, iron is often reported as simply iron rather than as ferric or ferrous iron. Likewise silica is commonly reported as  $\text{SiO}_2$ , although the actual form in solution is more likely to be  $\text{H}_2\text{SiO}_4$ . As a result the constituents are commonly reported using a mixture of terms, some nonionic such as iron, boron and silica and some ionic such as chloride, sulfate and bicarbonate. The references used throughout this study for the constituents will be those used by the U. S. Geological Survey.

Seven major ions are found in natural waters, and these account for practically all of the dissolved ionic concentration. Some of these ions may be paired or complexed with themselves or other ions, and this is discussed in Chapter 7. Table 2-1 shows the average distribution of the major ions in fresh water as given by Gorham (1961). The proportions of these ions vary greatly from stream to stream and even show some variation within the same stream. Some comparisons of these variations are made in Chapter 4.

Table 2-1

Average distribution of major ions in fresh water\*

Cations		Anions	
Calcium	64%	Bicarbonate	73%
Magnesium	17%	Sulfate	16%
Sodium	16%	Chloride	10%
Potassium	3%		

\*Percentages refer to the percentage of the total equivalents per liter. In addition to these seven ions, several other minor ionic and nonionic species may be of interest. Those included in this study are iron, silica, fluoride, nitrate and boron. Table 2-2 includes a more complete list of minor anions and cations found in natural waters (Powell, 1964).

Table 2-2

Minor inorganics

Cations		Anions
Aluminum	Cobalt	Fluoride
Iron	Arsenic	Nitrite
Manganese	Selenium	Bromide
Titanium	Cadmium	Phosphate
Chromium	Antimony	Boron
Nickel	Strontium	Iodide
Copper	Barium	Cyanide
Tin	Beryllium	Nitrate
Lead	Lithium	Carbonate
Zinc		

2.1.1 Silica. Silica refers to the oxide of the element silicon and is usually reported as parts per million of  $\text{SiO}_2$ . Silica, due to its molecular structure, presents a fundamental building unit for most rocks and minerals. As quartz, silica is a major constituent of many igneous rocks and sandstone, however, silica in the form of chert and opal is more soluble. Although silica is very abundant it also is quite insoluble and is usually found in concentrations of less than 40 parts per million in fresh water. But in volcanic areas it may be two or three times as high and in a very unusual case has been reported as high as 4000 parts per million (Feth et al., 1961).

It is generally believed that dissolved silica is in the form of silicic acid ( $\text{H}_4\text{SiO}_4$ , also written as  $\text{Si(OH)}_4$ ). The dissociation constant for this acid is

reported to range from  $10^{-9.41}$  to  $10^{-9.91}$  and as a result no appreciable dissociation occurs except at a high pH. That is, silica in natural waters typically exists in an uncharged form.

Silica causes no harmful effects to humans, fish, livestock, crops or most industrial processes. However, it is undesirable in boiler feed water because it tends to be deposited on the boiler tubes, and, if high concentrations exist in stream turbines, it is carried by the steam and deposits on the turbine blades.

2.1.2 Iron. Like silica, iron is commonly found in most rocks and soils and is relatively insoluble. The solution of iron by weathering processes is quite slow and due to solubility controls is not likely to account for much of the iron found in natural waters. Iron is an essential element for both plants and animals. The circulation of iron within the biosphere may account for most of the dissolved iron.

Iron is found as both ferric ( $Fe^{3+}$ ) and ferrous ( $Fe^{2+}$ ) in addition to forms complexed with organic or inorganic radicals. Although ferrous iron may be the most common form of iron in groundwater, it is unstable in the presence of oxygen and is readily oxidized to the ferric form which in turn tends to form strong complexes. Evidence suggests that most iron is in the form of organic ferric iron complexes (Hem, 1970).

The presence of iron in stream water is usually less than one part per million although it may be higher for groundwater or acid surface water. Iron is objectionable in water mainly because of tastes imparted to the water and the ability of iron solutions to stain laundry and porcelain. For irrigation purposes, iron provides no hazard.

2.1.3 Calcium. For most natural waters calcium is the main cation. For waters in contact with igneous or metamorphic rocks the concentration is generally low, but for those in contact with sedimentary rocks such as limestone, dolomite and gypsum the concentration can be very high. Calcium is found predominately as a simple divalent cation although organic and inorganic complexes occur. While organic complexes are probably not important, inorganic complexes primarily with bicarbonate and sulfate can account for a large percentage of the calcium present. Concentrations of calcium range from less than ten to several hundred parts per million. While calcium is a source of hardness and therefore objectionable, it is desirable in irrigation waters because calcium flocculates the soil and maintains good soil structure and permeability.

2.1.4 Magnesium. Magnesium is justifiable thought of as a "little brother" to calcium. It possesses many of the same characteristics and attributes. Like calcium the main sources of magnesium are sedimentary materials. Most magnesium in water results from solution of carbonate minerals. Magnesium however is not as abundant as calcium and is rarely as concentrated in solution. The ratio of magnesium to calcium is sometimes taken as a constant (Thomas et al., 1971) although this is not generally true. For a given stream the ratio of magnesium to calcium may easily vary by a factor of ten. Magnesium complexes with bicarbonate and sulfate ions are the most important. Magnesium also is a source of hardness and has

the same beneficial effects on soil structure as calcium. Magnesium has a laxative effect of persons not adapted to it, and for this reason, waters concentrated in magnesium are not recommended for use as drinking water supplies.

2.1.5 Sodium. Sodium is the most abundant of the alkali metals. Since sodium salts are very soluble, sodium once in solution tends to stay in solution. Most Sodium is the result of readily soluble sodium salt deposits found in nature as evaporate sediments. Sodium as a rule does not experience much complexing although bicarbonate and sulfate complexing can be significant. Concentrations of sodium in natural waters vary widely from only a few parts per million to as much as 100,000 parts per million (ten times that of sea water). Although excessive sodium concentrations are a hazard to both plants and animals, normally the main concern is their effect on agricultural soils. Unlike calcium and magnesium, sodium tends to disperse the soil colloids resulting in the destruction of flocculent soil structure. As an indication of the hazard due to high sodium waters, the sodium adsorption ratio (SAR) has been developed. Having the form of a mass-law equilibrium expression, the SAR indicates to a certain extent whether the irrigation water will, through ion exchange with the soil, tend to improve the soil (water high in calcium and magnesium) or degrade the soil (water low in calcium and magnesium).

$$SAR = \frac{meq/l Na^+}{\sqrt{\frac{meq/l Ca^{++} + meq/l Mg^{++}}{2}}} \quad (2-1)$$

Dividing points between very high, high, medium and low sodium hazards are SAR values of 26, 18 and 10.

2.1.6 Potassium. The main source of potassium is evaporate rocks which include potassium salts. Concentrations are rarely more than ten or twenty parts per million. For this reason, potassium is rarely of great concern.

2.1.7 Chloride. Chloride is one of the most abundant anions found in natural waters. Sedimentary rocks, particularly the evaporates, provide the main source of chloride. Chloride does not form any significant complexes in solution. At excessive concentrations chloride is a hazard, causing rapid corrosion in pipes and boilers and damaging crops. Chloride also interferes with many industrial processes. For municipal water supplies, the tastes imparted by the chloride rather than the actual health hazards dictate the acceptable chloride levels. Concentrations of chloride may range up to several thousand parts per million.

2.1.8 Sulfate. Dissolved sulfur is virtually all in the form of sulfate or one of the previously mentioned sulfate complexes. Most sulfate is derived from sedimentary rocks, but often a significant amount of the sulfate may be contributed by rainfall. Rainfall concentrations of more than ten parts per million have been observed. Sulfate contributes to corrosion, but is generally not a source of concern with respect to water quality until concentrations exceed several hundred parts per million. Sulfate

concentrations in natural water range from near zero to several thousand parts per million.

**2.1.9 Carbonate and Bicarbonate.** Along with chloride and sulfate, bicarbonate accounts for virtually all of the anions in solution. Carbonate and bicarbonate may be the result of dissolution of salts, or less important, as the result of an equilibrium reaction with dissolved carbon dioxide. The carbonate system is well discussed in many textbooks. The equilibrium between the carbon dioxide in the atmosphere and carbon dioxide in solution is rarely achieved due to the slow reaction rates involved. The content of dissolved carbon dioxide,  $H_2CO_3^*$  (the sum of aqueous carbon dioxide and  $H_2CO_3$ ), is of importance only in natural waters of low pH. On the other hand, carbonate ( $CO_3^{--}$ ) is of importance only for waters of high pH. By far the most prevalent carbonate species is the bicarbonate form ( $HCO_3^-$ ). The equilibrium reaction between the carbonate species is very rapid. Often, as is done in this study, the concentration of carbonate, which is hard to measure analytically, may be calculated using the pH and bicarbonate concentration. The relatively slow equilibrium reaction between carbon dioxide of the atmosphere and carbon dioxide in solution tends to limit the bicarbonate concentration. Surface waters rarely have more than 200 parts per million of bicarbonate, while groundwater which is not affected by the atmosphere may have over 1,000 parts per million.

**2.1.10 Other Species.** Other species of importance include fluoride, phosphates, nitrate and boron. Phosphate and nitrate are utilized by plants and are important indicators of the nutritive value of irrigation water or the susceptibility of natural waters to algal blooms and eutrophication. Boron, although essential for plant growth, is a hazard to many crops if the concentration exceeds one or two parts per million. Fluoride by acting as a decay preventative is beneficial in small concentrations but in concentrations of more than a few parts per million becomes harmful.

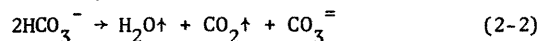
A great many other species are of importance to water quality. These however are not discussed in this study. Included in these are manganese, various alkali metals, alkaline earths, other trace metals and some nonmetallic, radioactive and organic constituents. These minor or "trace" constituents are generally found in quantities less than one part per million. Although often hard to detect and usually not present in sufficient concentrations to be of concern, many of these substances are toxic to plants and animals at very low concentrations.

## 2.2 Chemical Properties

Many of the quality characteristics of water are described in terms of properties. A property describes one particular aspect of the quality which is of interest.

**2.2.1 Dissolved Solids.** Dissolved solids are usually expressed as total dissolved solids and reported in terms of parts per million concentration. There are two ways of determining the total dissolved solids. The first is by weighing the residue after evaporation of a sample at 180°F. At this temperature

the bicarbonate present is converted to carbonate, carbon dioxide and water vapor according to Equation 2-2, and as a result only a portion of the bicarbonate weight is actually measured.



The second method is to simply sum the constituents determined by chemical analysis with the exception of bicarbonate which must be divided by a factor of 2.03 to give its equivalent weight as carbonate in accordance with the reaction given by Equation 2-2.

**2.2.2 Specific Conductance.** Specific conductance is a measure of the ability of a solution to carry an electrical current and as such is also an indication of the total salt content. A more complete discussion of this property is given in Chapter 7.

**2.2.3 pH.** The negative logarithm (base 10) of the hydrogen ion concentration, or more correctly the hydrogen ion activity, is called the pH. A pH of 7 indicates equal concentrations of hydrogen and hydroxyl ions, while a smaller pH value indicates an excess of hydrogen ion, and a larger pH value indicates the opposite. The pH value is important because the hydrogen ion concentration often determines what sort of reactions may take place and the form of the products. Most waters in the United States have pH values between 6.0 and 8.5, with groundwaters generally more acidic than surface waters (Powell, 1964).

**2.2.4 Other Properties.** Other properties which are of interest in natural waters include hardness, alkalinity, acidity, color, turbidity, taste, odor, oxygen demand and temperature. For a discussion of these and other properties the reader is referred to the references mentioned in the first section of this chapter.

## 2.3 Methods of Checking Chemical Analyses

Presently there are three methods of checking the overall accuracy of a chemical analysis of an aqueous solution. The most common is to sum and compare the total equivalents of anions and cations. This charge balance, however, is often used to determine one of the constituents by knowing the others, usually sodium plus potassium. Where all of the constituents have been determined without using the charge balance, this test will indicate when a major error has occurred in the analysis. The American Public Health Association et al. (1965) recommends that a recheck of at least one if not all of the determinations be done if the charge balance is not within acceptable limits, given by the equation:

$$\begin{aligned} & \Sigma \text{ meq/l anions} - \Sigma \text{ meq/l cations} \\ & = + (0.1065 + 0.0155 \Sigma \text{ meq/l anions}). \end{aligned} \quad (2-3)$$

This criterion is reported to be plus or minus one standard deviation of the errors for analyses made by an average chemist or analyst. Obviously, some analysts would consistently do better and some do worse. In this study, those chemical analyses which did not meet this criteria were routinely eliminated. It is possible, however, that compensating errors circumvent this approach.

A second method of checking is to determine the total dissolved solids both as a residue and by calculation from the determined concentrations. While this

will point out gross errors or the presence of a constituent which has not been determined, the presence of organic substances or water of hydration may make this only a rough check.

Rossum (1949) proposed a conductance method of checking analyses which is commonly used. This method requires the dilution of the solution to a specific

concentration and then the measurement of the conductivity. By calculating the conductance by using semi-empirical factors, a check may be made with the measured value. This method is more fully described in Chapter 7. An extension of Rossum's method is made in Chapter 7 so that the conductance for an undiluted sample may be calculated and checked against the measured conductance.

## Chapter 3 REVIEW OF PREVIOUS STUDY OF THE DISCHARGE-QUALITY RELATIONSHIP

This chapter is a brief review of work done by other researchers in the area of discharge-quality relationships. The primary purpose of the review is to provide a basis upon which reasonable models may be hypothesized, tested and interpreted. The review will also permit meaningful comparisons to be made between the approaches and results of this study and those of previous studies.

### 3.1. Introductory Remarks

Numerous studies have been made of the relationship between streamflow and the water quality in streams. These studies have varied from simple graphical representations to more complex mathematical modeling. A graphical representation of the relation between inorganic water quality and stream discharge is included in practically all stream studies which consider the quality of the stream water. Examples of graphical representations are numerous and include Hembree and Rainwater (1964), Hembree et al. (1964), Irons et al. (1965), Hughes and Leifeste (1965) and Keller (1967). The interest in the discharge-quality relation has been sufficient to encourage advanced studies beyond individual graphical presentations. The more advanced studies which have been made will be individually discussed in the next section. In examining the more advanced studies, which generally consist of fitting discharge-quality relationships to observed data, a number of limitations may readily be observed. Despite the number of studies, no single approach has been accepted for general usage. In addition comparisons between the various approaches have been few and inconclusive. The scope of previous studies has generally been very limited. Most often, only one stream using a very limited number of constituents or quality parameters was studied. In the closing section of this chapter these limitations will be further discussed, particularly in regard to steps taken in this study to improve the situation.

### 3.2 Previous Work by Others

Lenz and Sawyer (1944) endeavored to estimate streamflow from alkalinity measurements. In studying the pollution of the Madison Lakes, they discovered that measurement of flow into the lakes was difficult due to the marsh-like nature of the tributaries. There was not sufficient head to allow flume measurements without severely disturbing groundwater levels and the natural runoff pattern. In addition, the backwater effect of the lakes prevented the use of the stage-discharge relationships. Through the creation and use of alkalinity-discharge rating curves, as shown in Figure 3-1, the authors found that alkalinity measurements provided adequate flow estimates. It should be noted that only one rating curve was used for all of the tributaries with flow expressed per unit area. Seasonal corrections were found to be necessary for low flows less than 0.8 cfs per square mile. Seasonal variations were felt to indicate the presence of seasonal groundwater variations. Corrections were determined by plotting the observed deviations against time of year and drawing a smooth curve through the points. The correction factors for three of the creeks are shown in the article and all three show similar seasonal effects.

In investigating several southwestern streams Hem (1948) found that concentrations of dissolved solids are highly periodic on an annual basis as a result of the strong negative correlation between flow and conductivity. In further study of the hourly variation of flow and chloride concentration, he found that the two series experienced large diurnal variations. Both negative and positive correlations between flow and concentration were found on an hourly basis for different streams. Negative correlations could be explained by the dilution effect while the positive correlations could be explained by evaporation and deposition of salts in the stream bed at low flows, with a resultant increase in salinity as the stream stage rises and dissolves the deposited salts.

Durum, in 1953, studied the salinity-discharge relationship for the Saline River in Kansas during the period 1945-1959. He found that the total chloride load, given by

$$L = Q C, \quad (3-1)$$

where  $Q$  is the flow and  $C$  is the concentration of chloride, was approximately a constant for all flow ranges. This hyperbolic relation results in a straight

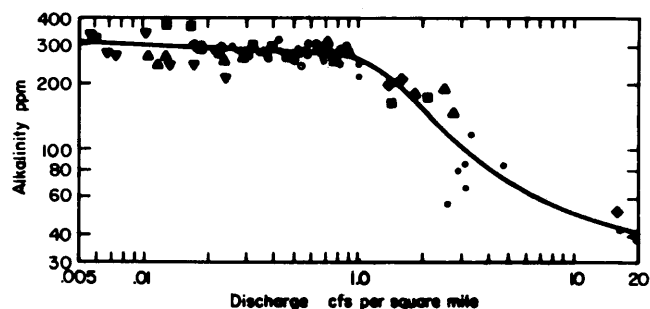


Figure 3-1. Alkalinity rating-curve for tributaries to Madison Lakes (after Lenz and Sawyer, 1944).

line plot of flow versus chloride concentration on logarithmic paper. For individual ions Durum also used the linear relation,

$$C_i = a + b\kappa \quad (3-2)$$

where  $C_i$  is the ion concentration in parts per million,  $a$  and  $b$  are regression coefficients, and  $\kappa$  is the specific conductance. This relation was used for chloride, sulfate, and the sum of calcium plus magnesium. His study showed that for these ions the proportions of the ions varied in a definite pattern with the total salinity. Bicarbonate concentrations were found to be more nearly constant for all flow rates. It was concluded that approximately 75 percent of the total annual dissolved solids discharge was from groundwater sources and only 25 percent from surface flow.

A major extension of the work of Durum was made by Ward (1958) who, using monthly values for the Arkansas and Red Rivers, found that dissolved

concentrations fit relations having a logarithmic form

$$\log C = a + b \log Q, \quad (3-3)$$

or parabolic logarithmic relationships

$$\log C = a + b \log Q + d(\log Q)^2, \quad (3-4)$$

in which C is the concentration of either sulfate, chloride, or dissolved solids, and a, b, and d are regression coefficients.

Ledbetter and Gloyna (1964) related individual ionic concentrations to conductivity through the use of equations of the form

$$C = a_k + b_k^2. \quad (3-5)$$

In applying this equation to the Red River near Gainesville, Texas and the Canadian River near Whitefield, Oklahoma, agreement was found for chloride and total dissolved solids with most of the variations accounted for by the first term. Sulfates, however, could not be explained by this approach. In relating concentrations to flow, Ledbetter and Gloyna propose the relationship

$$C = aQ^b, \quad (3-6)$$

where b is not a constant, but is given by

$$b = f + g \log Aq + hQ^n, \quad (3-7)$$

and C is an inorganic pollutant concentration, Q is flow, a, f, g, h and n are regression constants, and Aq is an antecedent flow index represented by

$$Aq = \sum_{i=1}^{30} \frac{Q_i}{i}, \quad (3-8)$$

where i is the number of days back from the present.

In a discussion of Ledbetter and Gloyna, Hart et al. (1964) suggest that the separation of groundwater flow, surface flow and interflow contributions to the total streamflow would result in a better quality-discharge relationship. They propose an equation of the form

$$C = a_1 Q_g^{b_1} + a_2 Q_i^{b_2} + a_3 Q_s^{b_3}, \quad (3-9)$$

where C is the inorganic concentration,  $Q_g$  is the groundwater flow,  $Q_i$  is the interflow,  $Q_s$  is the surface flow and the a's and b's are the regression coefficients. In an analysis of the Russian River at Hopland, California, Hart et al., report that an equation of this form was found to be applicable with the B coefficients set equal to unity, although they state that this would not be expected to be generally true.

Colby et al. (1956) in studying the Wind River at Riverton, Wyoming found using grouped data that the dissolved solids were highest at a flow of 400 cfs with lower values at both higher and lower flows. Similar results were obtained for the Bighorn River at

Thermopolis, Wyoming. The curve determined by Colby et al., for the Wind River is shown in Figure 3-2.

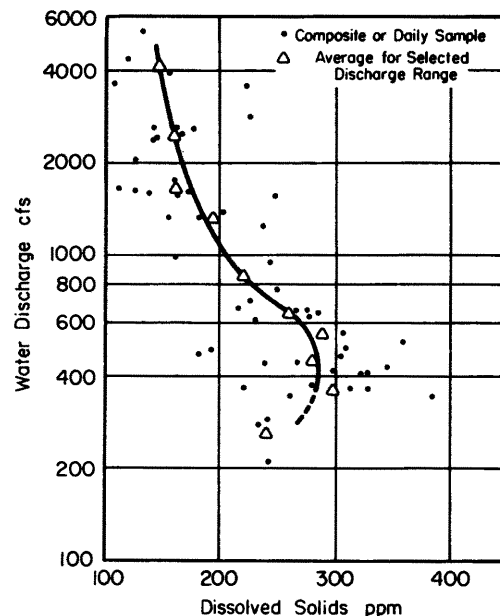


Figure 3-2. Relation of salinity to water discharge, Wind River at Riverton (after) Colby et al., 1956).

In studying a mountain creek, Korveh and Wilcox (1964), using the logarithmic transforms of flow and conductivity, related flow to conductivity, flow to pH and pH to conductivity by linear relations.

Langbein and Dawdy (1964), by consideration of Nernst's law obtained an equation identical in form to the dilution models later used by Johnson et al. (1969). This equation was stated as

$$C = \frac{S(1 + C_0 Q/DA)}{1 + QS/DA}, \quad (3-10)$$

where C is the inorganic pollution concentration, D is the maximum rate of dissolution per unit area, S is the concentration at saturation, A is the area,  $C_0$  is the rainfall concentration, and Q is the streamflow rate. By assuming the rainfall concentration was negligible, and relating mean annual runoff to median concentration of dissolved solids on 168 streams, a consistent relationship was found which could be fit by this equation in the form

$$C = \frac{a}{1 + bR}, \quad (3-11)$$

where R is the annual rainfall runoff and a and b are regression coefficients.

Supporting the findings of Lenz and Sawyer (1944), Hendrickson and Krieger (1964) also found that low flow concentrations were dependent on time of year. By examining low flow data for streams in Kentucky, they found that three discharge-concentration rating curves were needed to define the relationship: one for Spring and early Summer; one for late Summer and



more dilute than for late Summer and Fall and even more dilute than low flows for the Winter season.

In analyzing individual flood events Hendrickson and Krieger (1964) observed a loop effect. That is, a hysteresis effect was observed due to differing concentrations, as indicated by the conductivity, for the same flow on the rising and falling portions of the hydrograph. This relationship is shown in Figure 3-3 which indicates that concentrations tend to be higher

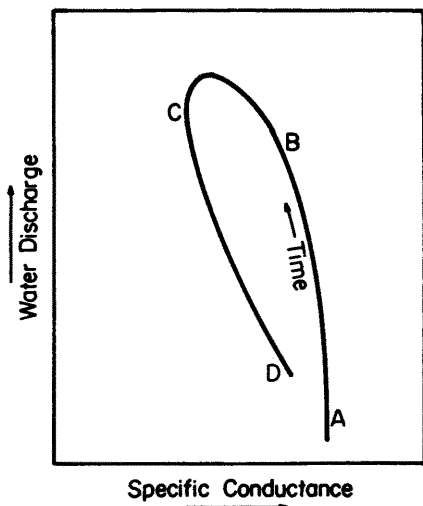


Figure 3-3. Relation between specific conductance and water discharge during a single flood (after Hendrickson and Krieger, 1964).

on the rising limb than on the falling limb of the flood hydrograph. The authors explain the process illustrated in the following manner. The cycle may be separated into three portions: a rising portion A to B, a peaking portion B to C and a falling portion C to D. At the start, point A, the flow is low and concentrated. As the flow increases the concentration changes relatively little due to the "old water" previously contained within the stream channel and also since the initial flood waters have washed away readily soluble weathered material from the soil. From B to C the concentration changes rapidly since the "old water" has now been washed from the channel and most readily soluble material has already been washed from the soil. During this same period the rise in stage tends to retard the highly concentrated groundwater inflow, thus further reducing the concentration in the floodwaters. During the final portion of the cycle, C to D, the discharge decreases and the concentration slowly reverts back to the original pre-flood concentration. As the stage falls, bank storage tends to move into the stream and groundwater once again contributes concentrated waters to the streamflow.

Toler (1965) working with Spring Creek in southwestern Georgia also found a cyclic relationship between discharge and dissolved solids concentration. However, unlike the results found by Hendrickson and Krieger (1964), Toler found that the concentrations were higher during the falling stage than during the rising stage of the same flood (Figure 3-4). This effect was attributed to a greater proportion of

groundwater discharge into the stream during the period of the falling stage. This was believed to be the result of rapidly responding groundwater levels and a good hydraulic connection between the groundwater and the stream.

On the Columbia River basin system, Gunnerson (1967), while finding basically the same straight line relations between the logarithms of flow and concentration (or hyperbola in cartesian coordinates), as Santos (1964), found previously, also noted that the

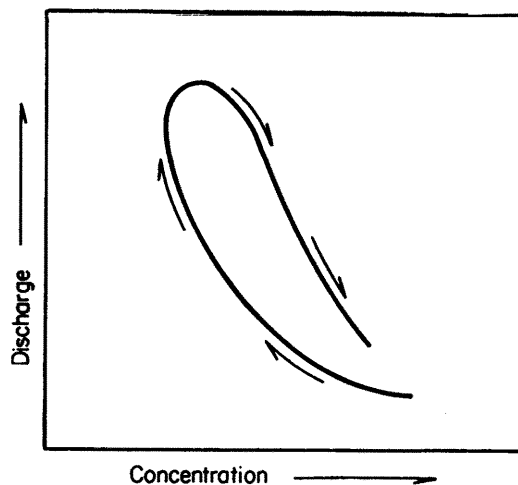


Figure 3-4. Idealized cyclic variation between water discharge and concentration of dissolved solids in Spring Creek (after Toler, 1965).

deviations were related to time of year. While somewhat difficult to interpret, several graphs similar to Figure 3-5 were presented which show that due to the

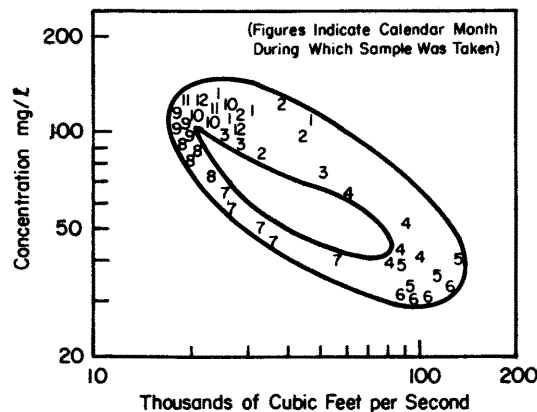


Figure 3-5. Total hardness related to streamflow, the Snake River at Wawawai, October 1961--September 1962 (after Gunnerson, 1967).

seasonal variation in flow and the flow-concentration relationship, the monthly mean values plot within a doughnut shaped area. Care must be taken to avoid the misinterpretation of these graphs as meaning that flow

and concentration are related by some elliptical relationship. This is not implied by the graphs. They do, however, show that the discharge-quality relationship is dependent on time of year.

Gunnerson explained these seasonal changes in the discharge-quality relationship as follows: During the early part of the rainy season, late Winter and early Spring, salts which have accumulated as the result of weathering are easily washed away, producing abnormally high concentrations. During late Spring the runoff is highest and the concentration lowest due to dilution. As the high flow season passes and the flow rate decreases, abnormally low concentrations are observed due to the "washed-out condition" of the watershed. As the low flow season continues the concentration increases to a peak as expected.

While similar results were obtained on the various streams studied, Gunnerson emphasizes the fact that each stream has its own "unique signature" of flow versus concentration. In reviewing logarithmic plots of concentration versus flow for nearly one hundred stations throughout the United States, Gunnerson noted a number of relationships have been observed including that of a linear logarithmic relation. For this case he classified the strength of the relationship based on the value of the slope.

In trying to estimate salinity from streamflow and vice versa on several small catchments in New Zealand and Switzerland, Keller (1967) obtained  $R^2$  (coefficient of determination) values from 0.64 to 0.95 using a linear logarithmic relationship.

In a rather complete but general discussion of the supply of major ions to streams and lakes, Gorham (1961) emphasizes the role of the atmosphere. Clark (1964) and others have argued that the atmospheric circulation of salts is of major concern. However, evidence by Van Denburgh and Feth (1956) tends to de-emphasize the role of the atmosphere. They found, in studying the chloride balance in western U.S. streams, that only 1.6 to 17 percent of the chloride removed by runoff originates in the rainfall. On the other hand Fisher et al. (1968) found that, for streams of the Hubbard Brook experimental forest, rainwater supplied most of the ionic constituents found in the streams. This discovery must however be tempered by the fact that the water quality is very good within these watersheds; so much so that the inorganic concentrations in the rainwater are comparable to those in the stream water. This unfortunately is generally not the case and particularly not the case for streams where salinity is a problem.

Johnson et al. (1969) in a continuation of the Hubbard Brook study examined the relationship between ion concentrations and stream discharge. In analyzing the various ions separately, they found that some increased with discharge while others decreased. They concluded that variations were explained best and most simply as a mixing of rainwater (or surface water) with deeper soil water. Applying an instantaneous complete mixing model with the assumption that the volume of surface water within the basin was directly proportional to the flow, they arrived at

$$C = \left[ \frac{1}{1 + AQ} \right] (C_g - C_s) + C_s, \quad (3-12)$$

where  $C$  is the concentration associated with the stream,  $Q$  is the discharge,  $C_g$  and  $C_s$  are constant groundwater and surface water concentrations and  $A$  is a constant inversely related to the groundwater storage volume. Due to the fact that the rainwater had a higher concentration of some ions, after accounting for evaporation, that the normal stream water, the concentrations of hydrogen ion, aluminum and nitrate were found to increase with discharge although the total salt content decreased with discharge. It was also found that the value of  $A$  in Equation 3-12 had to be varied by an order of magnitude to adequately account for all of the ions. The authors attributed this variation to "localized chemical effects."

Archer et al. (1968) used a simple mass balance mixing model for the Erie-Niagara basin of the form

$$C = \frac{Q_g C_g + Q_o C_o}{Q}, \quad (3-13)$$

where the stream concentration and flow are  $C$  and  $Q$ , the groundwater concentration and flow are  $C_g$  and  $Q_g$ , and the overland water concentration and flow are  $C_o$  and  $Q_o$ . In this application the overland and groundwater flows were estimated, and, by considering their concentrations constant, the stream concentration was estimated.

A basic assumption inherent in many of the approaches has been the concept that a process of groundwater dilution governs the stream-flow concentration. The problem has been reversed by Pinder and Jones (1969) and Visocky (1970) who estimated the groundwater component of flow from the conductance measurement. Both used the same basic equation

$$Q_g = \frac{(C - C_o) Q}{(C_g - C_o)}, \quad (3-14)$$

which may be easily obtained from Equation 3-13. It was found that the groundwater discharge could be estimated by considering the groundwater and direct inflow (overland flow) as having constant concentrations. Pinder and Jones point out the difficulties and inaccuracies of existing methods of separation of groundwater from total runoff and the ease of this method. They found that the results were consistent regardless of the ion or group of ions selected to predict the groundwater component. Visocky found that this method, while offering a simple alternative for use where observation wells are unavailable or rating curves are difficult to construct, gave lower estimates of the groundwater contribution than did the rating curve method.

In an attempt to determine the most efficient method to define the behavior of inorganic constituent concentrations in a stream, MacKichan and Stuthman (1969) undertook a study of the water quality-discharge relationship with their goal being to determine the length of record required to adequately define the water quality. While the study was cut short before its full completion the authors did realize and emphasize that the conductance measurement has a great potential for use in extending the usefulness of chemical analysis data. Their results also indicate

that the proportions of the various ions tend to remain fairly constant. Hem (1970) also points out that the proportions of ions tend to remain somewhat constant and as a result a linear relationship between the individual ion concentrations and the total dissolved solids or conductance (over limited concentrations ranges) is often observed.

In studying the relationships of dissolved ion concentrations to water discharge for the Pescadero Creek in California, Steele (1968) concluded that the well used linear logarithmic relationship,

$$\log \kappa = a \log Q + b, \quad (3-15)$$

fit the data. He determined the values of  $a$  and  $b$  by regression analysis. While the values of  $a$  and  $b$  could not be attributed to a single hydrologic effect, they were considered to represent the combined effects of numerous hydrologic factors. In a later study, Steele (1969) found that records of infrequent chemical analyses could not be used to determine annual values without serious errors. However, by using either daily conductivity or streamflow records and the relationships between the ions and either conductivity or streamflow, a better estimate could be made. In further studies, Steele and Gilroy (1971) found that long-term changes in salinity were due primarily to man's influence. The authors also indicate that trends in the discharge-quality relationship may be best determined by assuming a constant relationship and then analyzing the residuals for a trend over a period of time.

Sharp (1969, 1970) analyzed the time series of dissolved constituents for trend, cyclicity and oscillatory nature. He found positive correlation at full cycle and negative correlation at half cycle indicating annual cyclicity, evidence of trend with a positive slope and a positive correlation decreasing to zero with the lag.

By examining the proportions of ions (mainly calcium, sodium, chloride and bicarbonate) in solution for a large number of streams, lakes and oceans, Gibbs (1970) has proposed that three mechanisms control the chemical composition in streams. The three mechanisms are denoted as (1) atmospheric precipitation dominance, (2) rock and soil dominance, and (3) evaporation-chemical precipitation dominance. The waters of low salt concentration (20 to 30 ppm and lower) are classified as being dominated by salts supplied through atmospheric precipitation and are accordingly characterized by the major cation and anion being sodium and chloride, respectively. Those waters of very high concentration (1000 to 2000 ppm and higher) are considered to be formed through a process of evaporation and subsequent concentration of less concentrated waters. The proportions of the ions in this case are governed by the chemical precipitation of calcium carbonate from solution with the result being that sodium and chloride are the major ionic constituents. Rock dominated streams are supplied ionic constituents from the rocks and soil through which the water has passed on its way to the stream. They are characterized by a calcium bicarbonate dominated water chemistry and take on concentrations between the other two water types. Of course there are all degrees of mixture between the various mechanisms. As the salt concentrations increase from one stream to the next, the water type follows a general pattern going from a sodium chloride

to a calcium bicarbonate and back to a sodium chloride type water. However there is a large range in the proportions of the ionic constituents for a given concentration of dissolved solids. Some question (Feth, 1971) has been raised as to the quality of the data and the validity of the explanations given by Gibbs, however the general pattern shown by the ion proportions is undisputed.

In studying individual storms on streams in Oklahoma using time intervals of one hour and less, Pionke and Nicks (1970) found that the salinity rose sharply with the flow during the initial hydrograph rise and then fell sharply again to lower values. Their results tend to support the idea of an initial washout of the readily soluble material deposited by the evaporation of past solutions.

Hendrick (1970) in an unpublished study done at Colorado State University shows figures which tend to demonstrate that the proportions of various ions, while remaining fairly constant, do change in a definite relation to flow and total dissolved solids.

In a series of publications by Utah State University (Dixon et al., 1970; Hyatt et al., 1970; and Thomas et al., 1971) a flow-salinity simulation model developed for the Little Bear River system is described. Although a linear logarithmic relationship between flow and salinity was found to be superior, a semilogarithmic relationship was used, having the form

$$S = a + b \log Q, \quad (3-16)$$

where  $S$  is the salinity as measured by the specific conductance. However, when relating ion concentrations on a monthly basis, this relationship was not used. Average values were used for three ions, sodium, sulfate and chloride. Bicarbonate concentrations were estimated by the regression equation

$$[\text{HCO}_3] = aQ + bQ^2 + cQ^3 + dT + eQT + fQ^2T + gQT^2 + hT^2, \quad (3-17)$$

in which  $T$  refers to the month of the year and  $a$  through  $h$  are the regression coefficients. A charge balance was applied to determine the sum of calcium plus magnesium. Then, assuming that the ratio of calcium to magnesium remained constant at 1.63, these ions were also calculated.

Hall (1970, 1971) in a rather extensive two-part article discusses mixing models and their application to the dissolved solids-discharge relationship. In the first article he presents eight basic equations for the relationship, all based on mass balance concepts derived by making various assumptions. Hall states that the constants, while originally having meaning, lose their meaning due to the unrealistic assumptions necessary to arrive at workable equations. The results obtained are somewhat suspect since the validity of the assumptions is not known and the application of the equations to actual data gives far from conclusive results. In applying the eight equations to data from the Sleepers River subbasin and plotting the results on logarithmic coordinates, the eight curves are practically indistinguishable over the complete range of the data. This result clouds the issue of what the true relationship is and supports the principle that many functions with varying numbers of parameters may give equivalent results. The

actual form of a mathematical model may therefore be wrong, but if it gives equivalent results and utilizes fewer parameters or parameters which are easier to estimate, it may nevertheless be the best model for practical use. Hall offers a slightly different opinion by stating that the choice of a model in this case cannot be made on the basis of data alone but should be based on either known physical or chemical processes or additional data gathered with the purpose of selection in mind. The eight equations proposed by Hall are:

$$C = aQ^{-b} \quad (3-18)$$

$$C = aQ^{-b} + c \quad (3-19)$$

$$C = ae^{-bQ^c} \quad (3-20)$$

$$C = ae^{-bQ^c} + d \quad (3-21)$$

$$C = a - bQ^c \quad (3-22)$$

$$C = \frac{a}{1 + bQ^c} \quad (3-23)$$

$$C = \frac{a}{1 + bQ^c} + d, \quad (3-24)$$

where a, b, c and d are the regression coefficients which are allowed to take on only positive values in order to conform to the initial assumptions made in the derivations. Hall also found that the time of the year and the hysteresis effect produced deviations which interfered with the interpretation of results.

Hem (1970) provides a good general discussion of water quality in relation to stream discharge and discusses the application of mass balance models.

The breadth of discharge-pollutant studies was expanded by Manczak (1971) who considered pollution indices such as five day biochemical oxygen demand, permanganate, dissolved oxygen, phenol, anionic detergent and nonionic detergent, in addition to chlorides, sulfate, dissolved solids, total solids, various nitrogen species alkalinity, hardness and suspended solids. As expected all of these decreased with increasing flow except dissolved oxygen and suspended solids. He concluded that there are three basic curves of pollutant concentration versus flow as shown in Figure 3-6. Manczak also concluded that a basic requirement for an accurate relationship is that measurements be made simultaneously and preferably by continuously operating automatic water quality monitoring stations because of rapid fluctuations possible in both the discharge and pollutant levels.

Pionke et al. (1972) proposed a model for improving the relationships by considering a rough estimation of the groundwater component of flow. They found that significant improvement was possible for ephemeral streams by using their relationship rather than the relationship developed by Ledbetter and Gloyna (1964). The following equation was used by Pionke et al.:

$$\log C = a - b \log Q_b - c Q_s/Q_b, \quad (3-25)$$

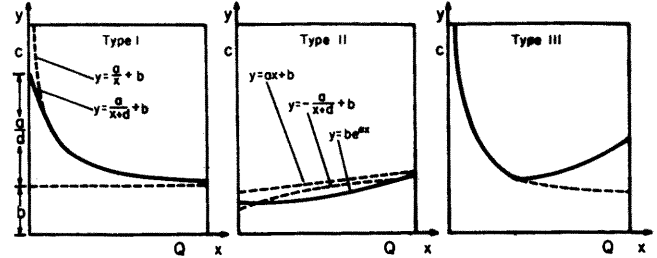


Figure 3-6. Basic types of curves representing correlation between concentration of pollutants and rate of flow. Type I--for heavily polluted rivers. Type II--for clean rivers. Type III--for intermediately polluted rivers (after Manczak, 1971).

where  $Q_b$  is the base flow,  $Q_s$  is the surface flow and a, b and c are derived by regression. The values of  $Q_b$  and  $Q_s$  are determined by separating the total flow Q into the two components as follows:

If  $\Delta Q > A$

$$Q_{b_i} = Q_{b_{i-1}} + A; \quad (3-26)$$

If  $\Delta Q < -A$

$$Q_{b_i} = Q_{b_{i-1}} - (0.05 \Delta Q); \quad (3-27)$$

and

$$Q_{s_i} = Q_i - Q_{b_i}, \quad (3-28)$$

where A is a constant, approximately two to five percent of the average annual flow.

Kennedy (1971) in studying silica concentration variations concluded that the concentrations varied in a consistent pattern with respect to the discharge and the total salt concentration as estimated by specific conductance. No mathematical model, however, was used. He also found that the silica concentration was often near equilibrium with some clays.

In an attempt to regionalize annual water quality characteristics, Steele and Jennings (1972) studied 31 stream water quality stations in Texas. They found that a single variable, either annual average stream discharge or average basin rainfall, would explain a significant part of the variance of water quality variables.

In a Master's thesis completed at the University of Nevada, Ward (1973) used the basic equation

$$C = aQ^b \quad (3-29)$$

in studying various inorganic water quality variables using 15 subbasins in the Carson River basin and related the values obtained for a and b with 65 basin characteristics. He concluded that the two most important basin characteristics were mineralization (mining activity) and density of roads.

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The studies made by other researchers concerning the relationship between discharge and inorganic water quality on a stream have taken numerous forms. As a result no single approach has been adopted for standard usage. In this study an attempt is made to compare a number of the proposed formulations and to select a basic relationship which may be expected to be generally applicable to natural streams.

In order to further justify the generality of the selected relationship, data from five streams will be used. This represents a significant improvement over past studies which were only concerned with one stream. Streams are selected as described in the next chapter to have a great deal of variety in terrain, vegetation, soil conditions, and water types. By selecting a number of streams having significant differences in water quality characteristics and applying the same basic

approach to each, the validity of proposed relationships for general usage is supported.

In order to broaden the approach, a number of dissolved constituents are studied. Past research has often been limited in scope to only one or two constituents and therefore only of moderate usefulness. By studying all of the constituents commonly determined by the U.S. Geological Survey the results of this study will be of greater general interest and usefulness.

The effect of time of year upon the discharge-quality relationship, although generally recognized as important, has largely been ignored or treated in a subjective manner by previous researchers. In this study a general objective approach towards this important aspect will be proposed.

## Chapter 4 DATA DESCRIPTION

A brief description is given of the available data and the data selected for this study.

### 4.1 Data Availability

The United States Geological Survey makes flow and chemical analyses measurements on numerous streams in the United States. This is the source of all data used in this study.

Inorganic water quality data provided by the U.S. Geological Survey usually includes the following, although at times other variables are included: mean daily discharge, silica, iron, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, fluoride, nitrate, boron, dissolved solids, hardness (calcium-magnesium and non-carbonate), sodium absorption ratio (or percent sodium), specific conductance, pH, and color. Unfortunately, often the chemical analyses are not complete and lack one or more of the major ions. Also series of chemical analyses are typically short and discontinuous.

Conductivity data are usually quite good, often for many more years than the stream's chemical analyses data. Conductivity is usually measured once daily and recorded with units of micromhos per centimeter ( $\mu\Omega/\text{cm}$ ).

Discharge measurements are continuous for many more years than either conductivity measurements or chemical analyses.

### 4.2 Units Reported

Chemical analyses are usually reported by the U.S. Geological Survey as parts per million, although parts per billion are also used for some trace constituents. For use in this study the units are generally converted to milli equivalents per liter for ionic components and milli moles per liter for nonionic components.

### 4.3 Sampling Techniques

Sampling for chemical analyses is usually done on a composite basis. Samples may be either time or discharge composited although the latter is by far the most common approach. In compositing samples, the individual daily samples are grouped so that similar samples are in one composite. Discharge and conductivity are the main criteria for making the choice of compositing time intervals, with discharge given the most weight. Any other rapid change in appearance is considered cause for strating another compositing procedure may be found in Rainwater and Thatcher (1960).

### 4.4 Methods of Measurement

The methods of measurement are not of primary concern to this study; therefore, the reader is referred to Brown et al. (1970) for complete coverage of the techniques used by the U.S. Geological Survey. When judging the quality of the data and assessing the difficulties or lack of agreement in applying models, knowledge of the methods of measurement and the asso-

ciated errors are important. Hem (1970) has estimated that the accuracy of the analytical results for the major constituents to be within plus or minus two to ten percent of the actual concentrations.

### 4.5 Selection of Streams

In selecting the streams, three main criteria were used: (1) that the streams be relatively free of man's influence; (2) that the area be between 1,000 and 10,000 square miles; and (3) that adequate data be available.

Streams were considered to be relatively free of man's influences if only very small towns or villages were within the basin, large mining activities or other activities which would greatly alter the natural water chemistry were not apparent and irrigation activities, especially irrigation return flows, had only a minor influence. These requirements were difficult to satisfy and are admittedly subjective. As a result, a process of elimination was used to select five streams which meet these requirements as much as was feasible considering the other requirements.

The requirement that the basin area lie within a certain range was considered essential to insure that the results would be of significance. Very large basins were considered to be undesirable. Most large basins are highly affected by man's activities. In addition, copious past quality records are more common for very large basins, and quality determinations by chemical analysis are likely to be justified in the future for these large basins. On the other hand, very small basins are of interest but data is generally lacking.

Data desired include what is often referred to as "standard complete" chemical analyses. These analyses include recording of concentrations of silica, iron, calcium, magnesium, sodium, potassium, bicarbonate, carbonate, sulfate, chloride, fluoride and nitrate. The pH, instantaneous discharge, conductivity and temperature are also normally recorded. These data are the result of composite samples made up of individual daily samples. In addition daily conductivity and discharge measurements are considered necessary. The data requirements proved to be the most difficult criterion to meet. Mainly, the lack of complete chemical analyses limited the choice. Often the data for one or more of the major ions was lacking in virtually every chemical analyses performed at a given stream station. All of the National Hydrologic Benchmark Network (Cobb and Biesecker, 1971) stations were eliminated. These stations are part of a program started in 1968 and were chosen to provide data on streams almost completely free of man's activities. Unfortunately the chemical analyses data recorded for these streams are only on a monthly basis.

Five stream stations were chosen for use: Henry's Fork River at Linwood, Utah; New Fork River near Big Piney, Wyoming; Pecos River near Puerto de Luna, New Mexico; Saline River near Russell, Kansas; and Wind River at Riverton, Wyoming. Additional discharge data was obtained for the Wind River near Crowheart,

Wyoming. Although the data were almost entirely obtained from the U.S. Geological Survey data center located at Reston, Virginia, much of the data is also published in U.S. Geological Survey Water-Supply papers. Additional information concerning various stations are found in the U.S. Geological Survey publication, Catalog of Information on Water Data

(Curtis et al., 1969; Harris et al., 1969) which is issued periodically by the Office of Water Data Coordination (OWDC). Tables 4-1 and 4-2 give pertinent information concerning the five stream stations and the data obtained. The locations of the stations are shown on Figure 4-1. Individual drainage maps for the five stream stations are shown in Figures A4-1 through

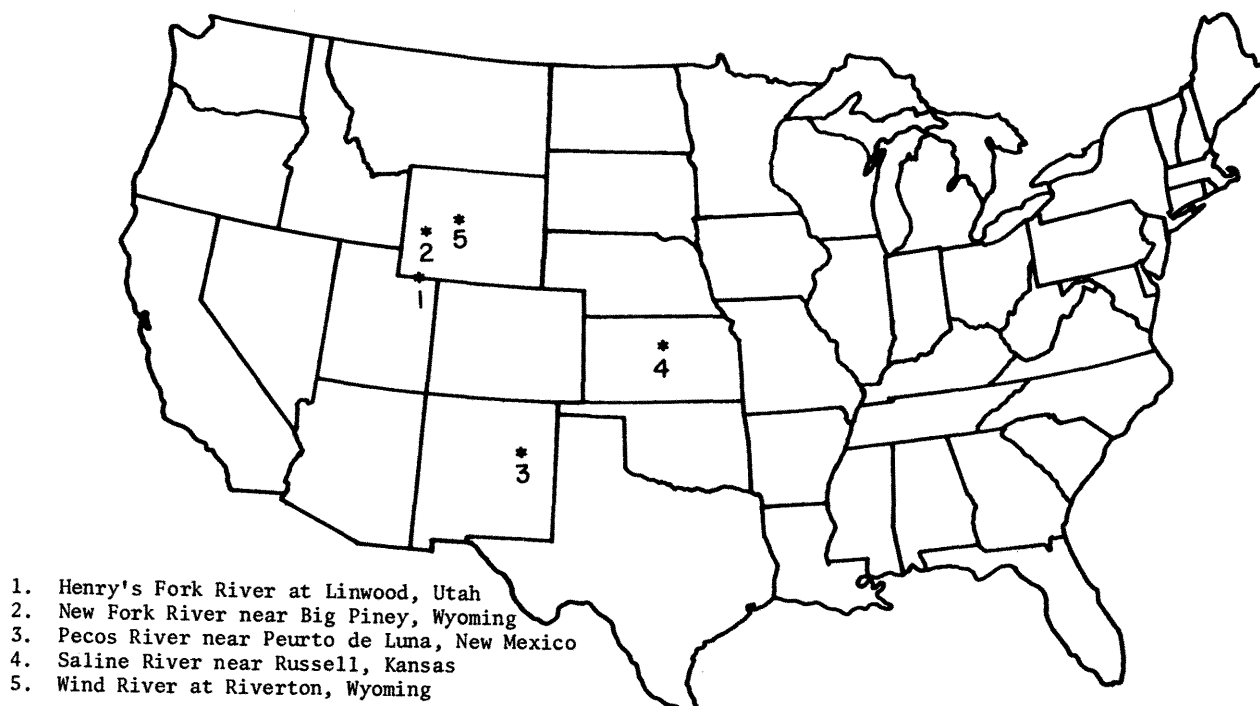


Figure 4-1. Location of selected stream stations.

Table 4-1. Basin area and location of selected stream stations.

Stream Station	Basin Area (sq mi)	Latitude	Longitude	State	OWDC* Number	USGS** Number	Records
Henry's Fork River at Linwood, Utah	520	41°00'45"	109°40'20"	Wyoming	04051 50935	09229500 09229500	Discharge Quality
New Fork River near Big Piney, Wyoming	1,230	42°34'	109°56'	Wyoming	04027 51059	09205000 09205000	Discharge Quality
Pecos River near Puerto de Luna, New Mexico	3,970	34°44'00"	104°31'30"	New Mex	04678 56384	08383500 08383500	Discharge Quality
Saline River near Russell, Kansas	1,502	38°58'00"	98°51'20"	Kansas	05776 50237	06867000 06867000	Discharge Quality
Wind River at Riverton, Wyoming	2,309	43°00'37"	108°22'35"	Wyoming	03931 51020	06228000 06228000	Discharge Quality
Wind River near Crowheart, Wyoming	1,891	43°14'33"	109°00'35"	Wyoming	03929	06225500	Discharge

\* Office of Water Data coordination

\*\* U.S. Geological Survey

Table 4-2. Quantities and type of data obtained.

<u>Stream</u>	<u>Type of Data</u>	<u>Amount of Data</u>	<u>Water Years*</u>
Henry's Fork River	Daily Conductivity	22 years	1950-1972
	Daily Discharge	44 years	1928-1971
	Chemical Samples**	378 samples	1959-1973
New Fork River	Daily Conductivity	4 years	1965-1968
	Daily Discharge	20 years	1953-1972
	Chemical Samples	126 samples	1965-1973
Pecos River	Daily Conductivity	2 years	1967-1968
	Daily Discharge	36 years	1937-1972
	Chemical Samples	136 samples	1967-1973
Saline River	Daily Conductivity	8 years	1945-1948 1965-1969
	Daily Discharge	23 years	1945-1952 1958-1972
	Chemical Samples	499 samples	1945-1973
Wind River (Riverton)	Daily Conductivity	8 years	1965-1972
	Daily Discharge	60 years	1911-1915 1917-1972
	Chemical Samples	370 samples	1947-1973
Wind River (Crowheart)	Daily Discharge	28 years	1945-1972

\* Water years beginning on October 1 of the year shown.

\*\* Chemical Samples are either discharge weighted composites or instantaneous (grab) samples.

A4-5 of the Appendix. The five streams selected have a variety of land forms, climates, vegetative covers and chemical characteristics. Each of these streams violates at least one part of the selection criteria to some degree. However, these five streams came closest to meeting the criteria of the streams considered for selection.

The Henry's Fork River, monitored at Linwood, drains a dendritic shaped basin located on the border between southern Wyoming and Utah. The river drains directly into the Flaming Gorge Reservoir on the Green River. Diversions for irrigation, transbasin diversions and some irrigation return flow affect the flow, particularly after 1969.

The New Fork River with a station near Big Piney is fed from a relatively round basin located in west-central Wyoming on the west slopes of the Continental Divide. Several small storage reservoirs and some irrigation (estimated 62,100 acres) affect the flow in the stream.

Fed by a slightly elongated dendritic basin, the Pecos River near Puerto do Luna has a monitoring station just above the Alamogordo Reservoir. Located in central New Mexico, the basin drains an area southeast of Santa Fe. The small town of Las Vegas (population 6307, 1970 census) is included in the far north portion of the drainage. This and irrigation of 12,500 to 17,500 acres are the major sources of influence which alter the natural water quality.

The Saline River, monitored at Russell, drains a very narrow, long basin with a length to width ration of approximately eight. Some irrigation takes place within the western Kansas basin.

Located adjacent to the New Fork drainage but on the opposite side of the Continental Divide, the Wind

River is fed by the most rugged terrain of the five streams. Most of the flow enters the stream in the upper reaches above the Crowheart station with little inflow between the Crowheart and the Riverton stations. Since considerable flow is diverted for irrigation between the two stations, discharge data was obtained for both stations for use with the quality data recorded for the Riverton station. The Riverton station is located just upstream of Riverton, Wyoming. Return flows from the irrigation waters diverted below Crowheart re-enter the stream below Riverton near or at Boysen Reservoir. Colby et al. (1956) have studied this basin in detail, with considerable emphasis on the chemical characteristics of the various tributaries to the Wind River.

#### 4.6 Closing Remarks

The data obtained is of good quality and is particularly well suited to this study. The five stream stations selected show a great deal of variety in basin area, topography, climate, drainage pattern, vegetation, stream discharge and chemical characteristics. As shown in Table 4-1, the areas of the basins range from slightly over five hundred square miles to nearly four thousand square miles. The basins are located in both mountainous and flat terrains, and Northern and Southern climates. Basins are included from both sides of the Continental Divide. As depicted in the basin maps contained in Figures A4-1 through A4-5 of the Appendix, the basin shapes and drainage patterns also show significant variety.

Typical chemical analyses data for each of the five streams are included in Table A4-1 of the appendix and give some indication of the variability in the basic data. In addition Table 4-3 indicates the range of variation in the daily data for discharge and conductivity. The conductivity data and the relationships between conductivity and discharge are further studied in Chapter 5.



Table 4-3. Discharge and chemical characteristics for the selected streams during a typical year.

<u>Stream</u>	<u>Year*</u>	<u>Quantity</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>
Henry's Fork River	1964	Discharge	3,780	2.7	243
		Conductivity	1,730	445	1,000
New Fork River	1967	Discharge	5,910	165	819
		Conductivity	289	58	196
Pecos River	1968	Discharge	7,500	72	224
		Conductivity	2,850	513	2,335
Saline River	1965	Discharge	1,750	1.2	57.2
		Conductivity	11,800	325	3,665
Wind River (Riverton)	1968	Discharge	3,280	84	582
		Conductivity	622	166	359
Wind River (Crowheart)	1968	Discharge	4,580	350	1,230

\* Water year beginning October 1 of the year indicated.  
Discharge in cfs; conductivity in ( $\mu\Omega$ /cm).

Table 4-4. Major\* cations and anions for the selected streams.

<u>Stream</u>	<u>Major Cation</u>	<u>Major Anion</u>
Henry's Fork River	Calcium	Sulfate
New Fork River	Calcium	Bicarbonate
Pecos River	Calcium	Sulfate
Saline River (low flows) (high flows)	Sodium Calcium	Chloride Bicarbonate
Wind River	Calcium	Bicarbonate

\* Major in the sense of greatest proportion of total cations or anions in terms of meq/l.

The major cation and major anion for each of the five stations selected are indicated in Table 4-4. For the Saline River, the major cation and major anion change from sodium and chloride at low flow to calcium and bicarbonate at high flow. The behavior is somewhat predicted by the general theories regarding the mechanisms governing water chemistry which were presented by Gibbs (1970). Although the Saline River data show large variations in the ion proportions, the data for the other four streams shows only slight variations in the ion proportions. In all cases the variation in the ion proportions was found to be small compared to the variation in the ion concentrations. By comparing the variance in the logarithms of the ion proportions with the variance in the logarithms of the ion concentrations for the major cation and major

anion, this author found that the variance for the ion concentrations averaged approximately an order of magnitude greater than the variance for the ion proportions. The fact that the ion proportions do not vary a great deal is not surprising. Hem (1970) has pointed out that, in much of the literature, the ion ratios for a given stream's water were considered to be constant with the variations in concentration due only to a dilution effect. Obviously this was an oversimplification; however, it is not hard to find examples where ion ratios have been taken as constants. Although ion ratios or ion proportions are rarely if ever constant, they often have been found to show only minor variations (MacKichan and Stuthman, 1969; Hendrick, 1970). The ion proportions will be further studied in Chapter 6.

## Chapter 5 CONDUCTIVITY AS RELATED TO HYDROLOGIC VARIABLES

This chapter deals with the relationships between conductivity and hydrologic variables. In this study the only hydrologic variables considered were the flow series and time of year although other variables such as water temperature, air temperature and effective evaporation also could have been considered. In this chapter conductivity will be treated as a measure of the total concentration of inorganic dissolved solids and as such will frequently be referred to as salt concentration or simply concentration.

The purpose of this chapter is to develop a form for the discharge-conductivity relationship which may be applied generally to natural streams. The use of daily data along with the generality of approach is an improvement over past studies.

The first two sections of the chapter deal with a discussion of a priori expectations and the derivation of an ideal model. Although the ideal model is too complex to be of practical use, it does provide insight into what should be considered. Dismissing the ideal model as too complex, a practical approach is selected for use. This approach consists essentially of the selection of the basic form of the discharge-conductivity relationship, with subsequent study of trends, periodicity, antecedent effects, and stochastic components. A split sample approach is used to further justify the validity of the approach taken.

### 5.1 A Priori Expectations

In examining the relationship of inorganic water quality to streamflow and time of year it is helpful to first consider what relationships might reasonably be expected. The results obtained by other researchers (Chapter 3), a knowledge of physical processes, and common sense contribute to these expectations.

The relationship between salt concentration and hydrologic variables can be considered to be made up of two parts: a deterministic part  $D(Q,T)$  which is a function of flow rate, time and any other hydrologic variables; and a stochastic part  $E$  which, although not predictable, may have a probability distribution whose parameters are a function of hydrologic variables. Therefore, a general equation may be written for the concentration:

$$C = D(Q,T) + E \quad (5-1)$$

The deterministic part of the model is of primary concern. For predictive purposes the stochastic term can be neglected, while for simulation purposes it must be included to preserve the characteristics of the concentration series. In this study prediction is interpreted as forecasting or estimation and therefore gives an estimate of what is expected. The intent of prediction is to obtain the best possible estimates. Simulation is used to mimic or reproduce an entire time series, preserving the population characteristics as much as possible. These characteristics include the stochastic variation about the estimate and the autoregressive nature of the time series of the stochastic components.

The deterministic proportion would be expected to follow either a basic equation such as

$$C = aQ^b \quad , \quad (5-2)$$

where  $a$  and  $b$  are regression coefficients as first used by Ward (1958) or a dilution model such as

$$C = \frac{a}{1 + bQ} + c \quad , \quad (5-3)$$

proposed by Johnson et al. (1969). The linear logarithmic relationship of Equation 5-2, while easy to apply, has the disadvantage that it does not have an upper limit and has a lower limit of zero which may not always be reasonable. For these reasons the mixing model has intuitive appeal since it has both upper and lower limits to which physical significance may be attached.

Alternative equations may also be developed based on chemical weathering models, mixing models under various assumptions (Hall, 1970), or groundwater residence time. Many of these equations are either similar in form or have been shown to fit data in a similar manner (Hall, 1971).

Once the basic form of the relationship between flow and concentration is obtained, the effect of time of year must be considered. The time of year may result in periodic parameters of the basic equation, the addition of a periodic term or only a modification for certain flow ranges such as was found for low flows by Lenz and Sawyer (1944) and Hendrickson and Krieger (1964). These three possibilities are illustrated below using Equation 5-2 as an example:

Periodic parameters,

$$C = a_{\tau} Q^{b_{\tau}} \quad ; \quad (5-4)$$

Addition of a periodic term,

$$C = aQ^b + c_{\tau} \quad ; \quad (5-5)$$

Flow range separation,

$$C = aQ^b \quad \text{for } Q > Q_0 \quad \text{and} \\ C = aQ^b + c_{\tau} \quad Q < Q_0 \quad , \quad (5-6)$$

where the subscript  $\tau$  signifies a periodic variable. There is reason to suspect a time variant relationship. The dissolution of matter is a chemical reaction whose rate is influenced by temperature, which in turn varies with the annual cycle. Both flow and concentration are periodic, and therefore it is logical to expect the relationship to also be periodic. Johnson et al. (1969) has found that the growing season affects the constituents found in streamflow while Gunnerson (1967) has found the same basic periodic pattern repeated in discharge-concentration graphs for several rivers of the Columbia Basin. There is more than adequate evidence to support the search for a periodic component.

There may also be trends or jumps within the relationship. Gradually increasing land use, with urbanization, irrigation and farming may produce a trend with gradual changes in the quality variables for the same discharge rate. Construction of dams and sewage treatments plants or the occurrence of forest fires and similar sudden changes may bring about sudden jumps in the relation between concentration and flow.

Cyclic or hysteresis effects may also exist. The formation of salt solutions through weathering and their subsequent evaporation may produce an intense initial peak in concentration with the next substantial storm. This "short-time" washout effect, which was observed by Pionke and Nicks (1970), appears very likely to occur on time intervals less than some characteristic time (probably of the same magnitude as the basin response time). On a larger time increment other effects may be observed. The effects of antecedent flow, "old water" in the surface water and groundwater systems and changes in the proportions of surface water and groundwater may account for loop effects similar to those observed by Hendrickson and Krieger (1964).

The stochastic component of Equation 5-1 may also be worthy of study. It logically may be expected to be serially dependent and is most likely to have a probability distribution whose parameters are partly a function of discharge and time of year. The stochastic component can be expected to be fairly large simply because the conductivity measurements are made only once per day rather than continuously. Since both flow and concentration may vary widely during a day, the correlation of an instantaneous value of concentration with an average value of flow should not be expected to be as high as with commensurate values.

### 5.2 An Ideal Model

An ideal model would be expected to take into account all of the effects mentioned in the previous section. On a short time scale, the response to a flood event would be expected to be as shown in Figure 5-1, with a washout of readily soluble salts during the initial stages and a clockwise loop effect due to the changing proportions of groundwater and surface water and the antecedent effects caused by storage within the groundwater and surface water systems.

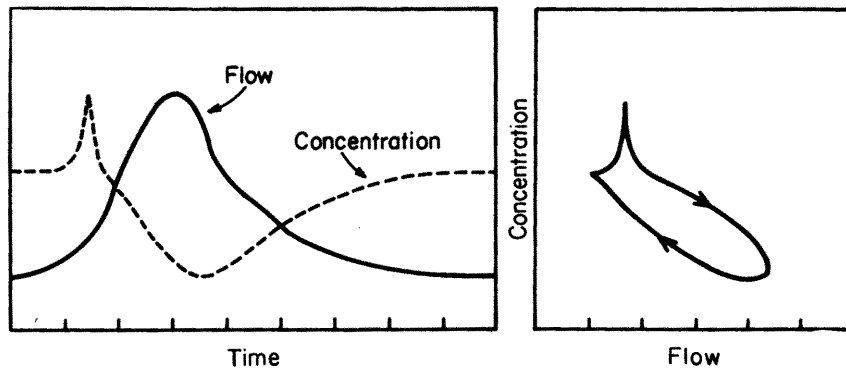


Figure 5-1. Quality response to flood events on a small time scale.

On a larger time scale the effect of time of year would become apparent. The high flow season would be characterized by a lower salt concentration in the groundwater due to the relatively short residence time and, therefore, generally lower concentration for the stream itself. This effect would be the result of gradual changes in the groundwater quality due to prolonged changes in the quantity of flow (Figure 5-2).

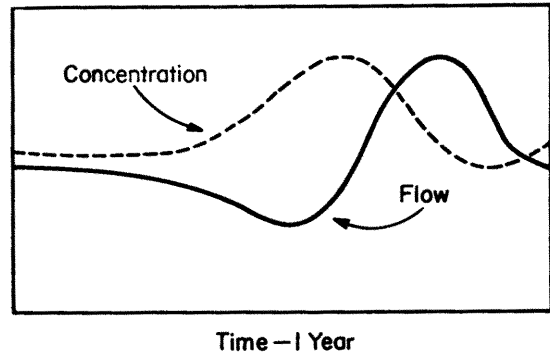


Figure 5-2. Groundwater flow and quality response to seasonal cycles.

In addition, on an annual time scale the surface water dissolution process varies. Plant activity, temperature, the possibility of snow cover, and the weathering process are all dependent on season and influence the quality of the surface runoff.

In order to arrive at an ideal model, one would like to include the flow separation concepts of Hart et al. (1964), the dilution model with variable groundwater storage of Johnson et al. (1969), the mass balance concepts presented by Hem (1970), the chemical dissolution (Nernst's law) model of Langbein and Dawdy (1964), the flood event hysteresis effects found by Hendrickson and Krieger (1964), and the general effects of the time of year.

In separating the flow into three constituents, surface, groundwater and interflow, there are two mass balance equations available.

$$Q_t = Q_s + Q_g + Q_i \quad (5-7)$$

and

$$Q_t C_t = Q_s C_s + Q_g C_g + Q_i C_i ,$$

or

$$C_t = \frac{Q_s C_s + Q_g C_g + Q_i C_i}{Q_t} , \quad (5-8)$$

where the subscript t denotes total, s denotes surface, g denotes groundwater, and i denotes interflow. Generally the only measured variable is the total flow, except when the model is being calibrated and then the stream concentration is also measured. Therefore, the flow components must be determined from the streamflow series alone and a general model is necessary. In general each component is a function of the past streamflow series.

In broad terms

$$Q_g = f_1(Q_t) ,$$

$$Q_i = f_2(Q_t) ,$$

and

$$Q_s = Q_t - Q_g - Q_i . \quad (5-9)$$

A number of models for flow separation are possible, and while their accuracy may not be high, anyone may prove to be adequate.

The concentration of the groundwater and interflow water may logically be assumed to follow Nerst's law. Using the approach of Langbein and Dawdy (1964), for a given temperature the rate of solute dissolution, L, is given by

$$L = AD \left( \frac{S-C}{S} \right) , \quad (5-10)$$

where A is the area of contact, D is the maximum rate of dissolution possible, S is the saturation concentration, and C is the water's actual concentration. The rate of dissolution must equal the rate at which the solute is carried away, if the system is considered to be at steady state. Thus

$$Q(C - C_o) = AD \left( \frac{S-C}{S} \right) , \quad (5-11)$$

where  $C_o$  refers to the concentration entering the interflow or groundwater system. For the interflow system,  $C_o$  would be concentration of surface flow  $C_s$ , and for the groundwater system,  $C_o$  would be the interflow concentration  $C_i$ . Solving for the concentration,

$$C = \frac{S(1 + \frac{QC_o}{AD})}{1 + \frac{QS}{AD}} . \quad (5-12)$$

If the volume of the groundwater or interflow system is assumed to change proportionally with the flow (Johnson et al., 1969), the area of contact would also be expected to change with the flow, or

$$A = A^o + bQ . \quad (5-13)$$

While this approach appears to be applicable to groundwater and interflow waters, the concentration of salts in the surface flow would not be expected to follow this type of law, mainly because the surface water concentration is the result of dissolving salts deposited previously by either evaporating solutions or by mechanical weathering. The surface water concentration would be expected to be more a function of flow rate and particularly antecedent flows. If the antecedent flows have been very high the surface will have been washed clean of any soluble salts. On the other hand, if the antecedent flows have been low the available salts will be high as a result of weathering and subsequent dissolution and deposition due to evaporation. The surface flow concentration may be expected to be related to antecedent flow as shown in Figure 5-3, where the antecedent flow index  $A_q$  is a function of previous flows; for example

$$A_{q_i} = \sum_{j=1}^{\infty} a Q_{i-j}^b e^{-c \cdot j} . \quad (5-14)$$

The seasonal effect would be felt in the values of D of Equation 5-12 and a of Equation 5-14. The maximum rate of dissolution D is temperature dependent and thus time dependent. The time of year influences many aspects of surface weathering and also plant activity. Therefore seasonal variations in the parameter a of Equation 5-14 would be expected.

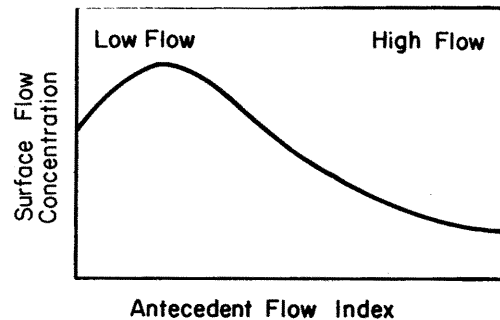


Figure 5-3. Ideal relationship of surface flow concentration to antecedent flow.

The order of calculation for this ideal model would proceed in the following manner:

1. Calculate the flow components  $Q_g$ ,  $Q_i$ , and  $Q_s$  by Equation 5-9;
2. Calculate the antecedent flow index  $A_q$  from Equation 5-14, and by using Figure 5-3, obtain the value of  $C_s$ ;
3. Calculate the value of  $C_i$  from Equation 5-12, using the appropriate values,

$$C_i = \frac{S_i \left( 1 + \frac{Q_i C_s}{A_i D_i} \right)}{1 + \frac{Q_i S_i}{A_i D_i}} ,$$

where  $A_i = A_i^O + b_i Q_i$ , and  $D_i$  is dependent on season of the year.

4. Similarly calculate  $C_g$  by

$$C_g = \frac{S_g \left(1 + \frac{Q_g C_i}{A D_g}\right)}{1 + \frac{Q_g S_g}{A D_g}}$$

5. Utilizing the values obtained for  $Q_g$ ,  $Q_i$ , and  $C_s$ , the stream concentration may be calculated by

$$C_t = \frac{Q_s C_s + Q_g C_g + Q_i C_i}{Q_t}$$

Although this ideal approach is appealing, the difficulties involved make it unworkable. The number of parameters and constants which must either be estimated or assumed cause this approach to be rejected. Since the entire concentration series is considered to be related only to time of year and the flow series, a more practical approach is to relate them directly. However, in this writer's opinion, if physical significance is to be maintained by the parameters, a high degree of complexity is unavoidable. To actually verify and test the accuracy of the parameters for the ideal model described would require a great deal of additional data not normally available and whose acquisition is not normally justified. To simplify the ideal model, for instance to a model of flow separation with constant groundwater and interflow concentrations, may impose unrealistic constraints on the problem and due to the inherent errors in the data and the errors involved in flow separation, would be difficult to justify.

### 5.3 Practical Approach Selected

The practical approach selected consists of five parts. The first is the selection of a basic equation for the relationship between flow and conductivity. Next analysis is made to test and remove trends in the relationship as indicated by the residuals. The third step is to analyze the effects of time of year by either adding a periodic term or by making the parameters themselves periodic. The next step is to assess the effects of antecedent flow and to model the hysteresis effect if noted. The final step is to analyze the resulting stochastic component.

The selection of a basic equation is accomplished primarily through the use of the Saline River data.

After the selection of the basic equation the next four steps are taken using the first ten years (1950-1959) of data for the Henry's Fork River and then the results are checked on the next ten years (1960-1969) of data for that stream. This split-sample approach is taken as a further verification of the basic equations. The final two years (1970-1971) of the Henry's Fork River data are reserved for use later with the complete model, in predicting and simulating the conductivity and ion concentrations in solution.

Following the split-sample analysis, equations are fit to all twenty years (1950-1969) of the Henry's Fork River data and also to all of the data for the other streams studied.

In regard to the Wind River, one additional aspect was examined. In studying the Wind River basin, it was noticed that a substantial amount of flow was removed by irrigation between Crowheart and Riverton. It was feared that this loss of flow would adversely affect the relationships. In order to study this aspect, both the flows at Crowheart and at Riverton were individually correlated with the conductivity measured at Riverton.

### 5.4 Selection of the Base Equation

In studying the literature, it is not clear what type of equation should be used as a base. Therefore, fourteen equations as shown in Table 5-1 were chosen for study and possible use. Equations chosen for study were adopted from those used by other researchers or as modifications or combinations of those used by them (Equation 5-15, Ward, 1958; 5-16 and 5-17, Ledbetter and Gloyna, 1964; 5-19, Langbein and Dawdy, 1964; 5-23 and 5-24, Dixon et al., 1971; 5-22, Durum, 1953; 5-18, 5-20, 5-21 and 5-26, Hall, 1970; 5-19, 5-22, 5-25 and 5-26, Manczak, 1971).

The fourteen equations of Table 5-1 were tested using conductivity data (see Table 4-2 for dates) of the Saline River. The average conductivity and average flow were calculated within intervals of flow ranging from 3.5 cfs to over 9000 cfs with a total of 37 intervals. Each interval involves the same logarithmic change in flow from the low value to the high value for the interval. Using these grouped data, a least squares fit was made of the equations. Figure 5-4 shows the grouped data used in fitting the equations. The 37 points are connected by straight lines. Figure 5-5 shows daily values for the month of November, also on the Saline River, and provides an indication of the variations in the individual daily values. Table 5-2 gives the resulting parameters for those equations which fit the data well. As shown, a number of the equations perform equally well. The errors appeared to be distributed randomly for all but Equations 5-19 and 5-26 when examined visually. In plotting both individual conductivity-flow samples and grouped data for all five streams, none of the data suggest any compelling reason to choose any particular one of the equations or to perform additional testing. Therefore, the choice of a basic equation is made on the basis of three factors: quality of fit, number of parameters, and ease of estimating the parameters. In this way, Equation 5-15 is chosen for further use. This equation also has the advantage of having been widely used by other researchers on a variety of streams.

In utilizing Equation 5-15, it is advantageous to rewrite the equation in a logarithmic form. This form has the advantage of being linear in the logarithms of the variables and therefore easily fit by a least squares linear regression upon the logarithms with the parameters easily identifiable as the slope and intercept for a logarithmic plot.

Equation 5-29 using base 10 logarithms will be the form used henceforth.

$$\log \kappa = a \log Q + b \quad (5-29)$$

Table 5-1. Conductivity-flow equations.

Power Equations:

$$\kappa = aQ^b \quad (5-15)$$

$$\kappa = aQ^b + c \quad (5-16)$$

$$\kappa = aQ^b Q^c \quad (5-17)$$

$$\kappa = aQ^b Q^c + d \quad (5-18)$$

Reciprocal Equations:

$$\kappa = \frac{1}{a + bQ} + c \quad (5-19)$$

$$\kappa = \frac{1}{a + bQ^c} \quad (5-20)$$

$$\kappa = \frac{1}{a + bQ^c} + d \quad (5-21)$$

$$\kappa = a + b/Q \quad (5-22)$$

Semilogarithmic Equations:

$$\kappa = a + b \log Q \quad (5-23)$$

Power Series Equations:

$$\kappa = aQ + bQ^2 + cQ^3 + d \quad (5-24)$$

Linear Equations:

$$\kappa = a + bQ \quad (5-25)$$

Exponential Equations:

$$\kappa = a 10^{bQ^c} \quad (5-26)$$

Combination Equations:

$$\kappa = aQ^b c^Q \quad (5-27)$$

$$\kappa = \frac{1}{a + bQ} + cQ^d + e \quad (5-28)$$

A least-squares regression on the logarithms of the variable is not the same as a least-squares regression on the untransformed variables. In an untransformed regression, errors are given the same weight regardless of the value of conductivity, so that high conductivity (low flow) values are given the most emphasis while the low conductivity (high flow) values are given very little emphasis. This type of regression may be superior if the high conductivities are of primary interest. With the logarithmic regression, errors have a multiplicative effect. In this case, the same percentage error has the same weight regardless of the value of conductivity. This type of logarithmic regression is generally superior over the normal linear regression for data where the percent error is of greater concern than the actual error. For example,

Conductivity,  $\mu\text{U}/\text{cm}$

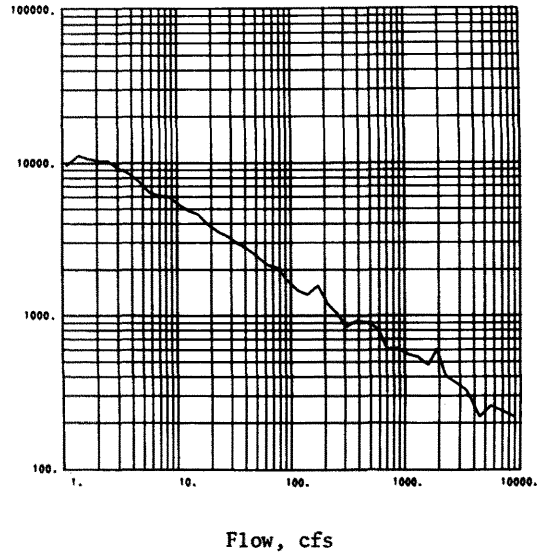


Figure 5-4. Grouped data of conductivity versus flow of the Saline River.

Conductivity,  $\mu\text{U}/\text{cm}$

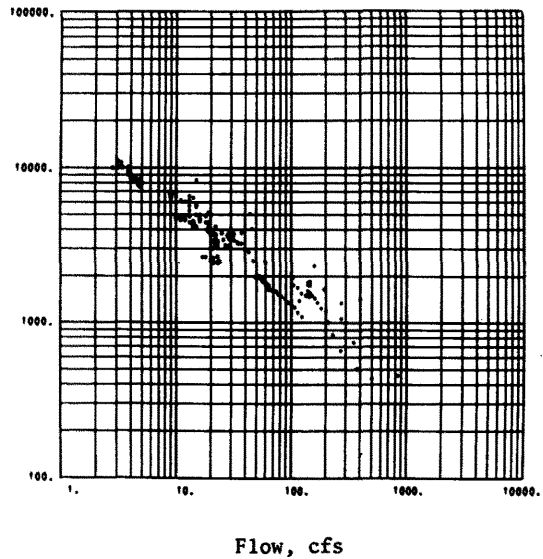


Figure 5-5. Conductivity versus flow of the Saline River for November data only.

Table 5-2. Parameters of conductivity-flow equations fit to grouped and averaged Saline River data.

<u>Equation</u>	<u>Parameters</u>	<u>Correlation Coefficient - R<sup>†</sup></u>
5-15	a = 15560. b = -0.4649	<u>≥ 0.99</u>
5-16	a = 15560. b = -0.4649 c = -42.72	<u>≥ 0.99</u>
5-17	a = 15148 b = -0.4462 c = 0.008866	<u>≥ 0.99</u>
5-18	a = 12670 b = -0.3790 c = 0.05025 d = 230.0	<u>≥ 0.99</u>
5-19	a = 1.023 x 10 <sup>-3</sup> b = 9.435 x 10 <sup>-6</sup> c = 538.4	<u>≥ 0.99</u>
5-20	a = 3.817 x 10 <sup>-6</sup> b = 6.146 x 10 <sup>-5</sup> c = 0.4788	<u>≥ 0.99</u>
5-21	a = 4.363 x 10 <sup>-6</sup> b = 6.132 x 10 <sup>-5</sup> c = 0.4757 d = -25.66	<u>≥ 0.99</u>
5-26	a = 17090. b = -0.2387 c = 0.3100	0.99
5-27	a = 15650 b = -0.4714 c = 0.9999	<u>≥ 0.99</u>
5-28	a = 4.464 x 10 <sup>-4</sup> b = 4.760 x 10 <sup>-5</sup> c = 11910. d = -0.4456 e = 18.20	<u>≥ 0.99</u>

† The correlation coefficients listed are for the grouped and averaged data points and must not be interpreted as those using daily data.

an error of 20  $\mu\text{U}/\text{cm}$  (micromhos per centimeter) is a large error if the measured conductivity is 40  $\mu\text{U}/\text{cm}$ , but is insignificant if the measured value is 4000  $\mu\text{U}/\text{cm}$ . On the other hand an error of 20 percent in a measured value of 40  $\mu\text{U}/\text{cm}$  is more nearly comparable in severity to an error of 20 percent in a measured value of 4000  $\mu\text{U}/\text{cm}$ . If an untransformed least squares were to be adopted, a 100 percent error in one data set could conceivably be given the same weight as a one percent error in another data set.

The logarithmic equation (5-29) has an additional advantage over many of the equations which were rejected. Regardless of what values are obtained for the parameters, the predicted value for the conductivity must be greater than zero.

A disadvantage overlooked by most investigators is that the predicted values given by a logarithmic regression are biased. While the logarithmic errors are unbiased and have a mean of zero about the

predicted values, the untransformed errors have a mean different from zero. If values are to be used for prediction, particularly for the estimation of averages such as mean annual values, corrections must be applied. In this study, corrections will be applied when making predictions but not when simulating conductivity time series. Generally the corrections are quite small, one or two percent, and could be neglected with little apparent effect. The procedure for correcting for the bias is covered in Chapter 8.

### 5.5 Trend Testing and Removal

The existence of a trend in the discharge-conductivity relationship as a result as of man's activities is possible. What is of concern is neither a trend in the flow series nor a trend in the conductivity series, but a trend in the relationship. The residual series resulting from the application of the basic equation is examined for evidence of a trend. A linear regression is made between the residual errors

and time. The existence of a trend is determined by a test of whether the parameters of fit are significantly different from zero.

No trends are found to be present in any of the five streams studied. If a trend had been found, it would have been removed from the conductivity series by the application of the following equation:

$$\log \kappa = \log \kappa_T - t_1 T + t_2, \quad (5-30)$$

where  $\kappa$  is the conductivity with the trend removed,  $\kappa_T$  is the original conductivity,  $T$  is the time and  $t_1$  and  $t_2$  are the parameters determined for the linear trend.

### 5.6 Variations to the Basic Equation

By considering seasonal effects, a number of variations in the basic discharge-conductivity relationship may be developed. The first variation is to consider the intercept term to be periodic. Thus

$$\log \kappa = a \log Q + b_T, \quad (5-31)$$

where  $b_T$  is now a periodic intercept term given by Fourier analysis and  $a$  is the constant slope term obtained earlier in fitting Equation 5-29. The use of a periodic intercept term is the natural result of the observation that both the means of the daily flow and conductivity series are periodic. Figures 5-6 and 5-7 illustrate the periodicity which is inherent in the means of the daily discharge and conductivity series.

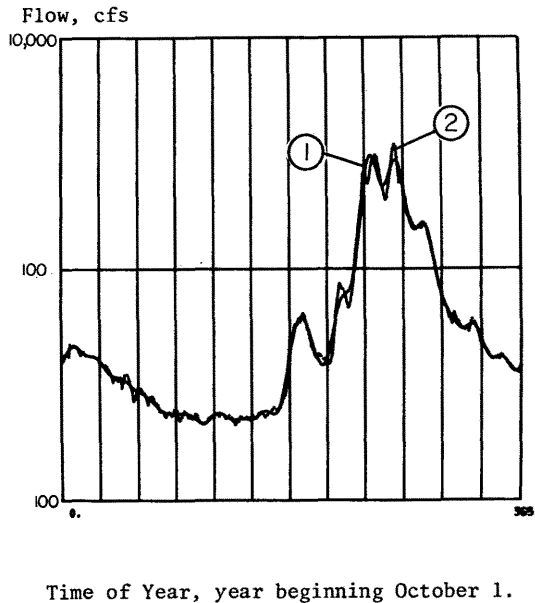


Figure 5-6. Harmonic fit of the means for the daily conductivities for the New Fork River. (1) fitted; (2) observed.

If the deviations from the means are considered, the following equation is obtained which reduces to Equation 5-31:

$$\log \kappa - (\overline{\log \kappa})_T = a[\log Q - (\overline{\log Q})_T] \quad (5-32)$$

The terms  $(\overline{\log \kappa})_T$  and  $(\overline{\log Q})_T$  refer to the periodic means of the log conductivity and log discharge respectively. The harmonic variation in the relationship may be illustrated by plots similar to those made by Gunnerson (1964). This is shown by Figure 5-8 where the fitted values for the daily mean discharge (Figure 5-6) are plotted against the fitted values for the daily mean conductivities (Figure 5-7) for the New Fork River. Unlike the results found by Gunnerson (1964), the conductivity is higher during the early Summer than the early Spring when the discharge is the same.

Noting that the use of the slope term developed in fitting Equation 5-29 is not strictly applicable in this case since it was obtained using a constant intercept, a more justifiable estimate for the slope term is desirable. By fitting the basic equation to data using several intervals within the year, a weighted average slope  $a_w$  is calculated. In finding the weighted average slope the weights used are the inverse of the estimates for the variance of the individual slopes. After obtaining the value for the weighted slope, the periodic intercept is calculated. Thus the second variation to the basic equation is

$$\log \kappa = a_w \log Q + b_T, \quad (5-33)$$

where  $a_w$  is the weighted slope and  $b_T$  is a periodic intercept, which is not the same as that of Equation 5-31.

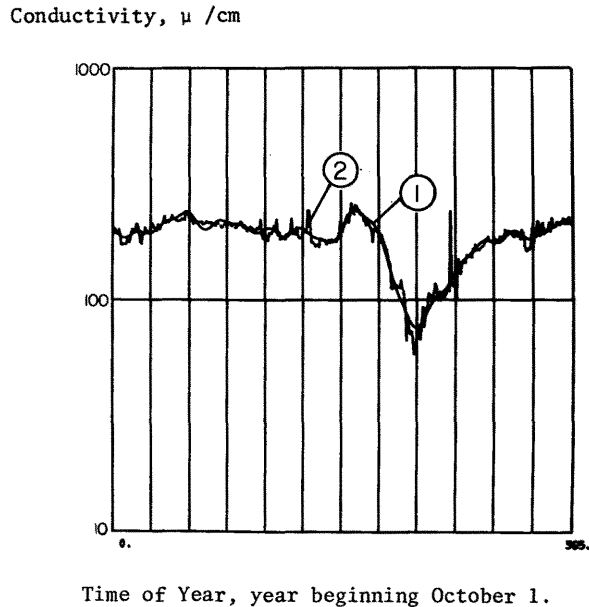


Figure 5-7. Harmonic fit of the means for the daily conductivities for the New Fork River. (1) fitted; (2) observed.

A third variation is to consider both the slope term and the intercept term as periodic. Thus,



$$\log \kappa = a_{\tau} \log Q + b_{\tau} , \quad (5-34)$$

Conductivity,  $\mu\text{U}/\text{cm}$

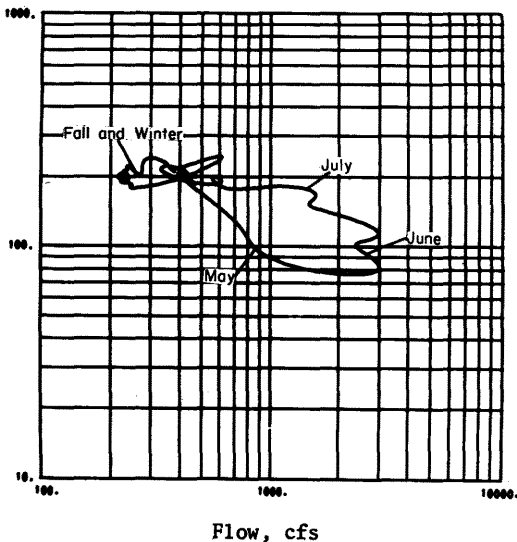


Figure 5-8. Periodic mean conductivity of Figure 5-7 versus the periodic mean flow of Figure 5-6, for the New Fork River.

where  $a_{\tau}$  and  $b_{\tau}$  are now the periodic slope and intercept terms. This form is reasonable since both slope and intercept terms were found to be significantly different for different intervals within the year.

In studying the periodic variations of the slope and intercept, two observations are made. First, slope and intercept estimates are not precise and the use of a large number of harmonics would not be justified. The second observation is that the slope and intercept terms are strongly related. It is found that most of the variation in the intercept term can be explained by the slope term using the linear equation

$$b_{\tau} = -c_1 a_{\tau} + c_2 + d_{\tau} . \quad (5-35)$$

Although the linear relationship explains most of the variation in the intercept, a small periodic term  $d_{\tau}$  is still required. In applying the results of Equation 5-35 to Equation 5-34 the following equation results:

$$\log \kappa = a_{\tau} (\log Q - c_1) + c_2 + d_{\tau} . \quad (5-36)$$

By neglecting the small periodic term  $d_{\tau}$ , a significant result is obtained. No matter what time of year, the relationship tends to go through the same point ( $\log \kappa = c_2$ ,  $\log Q = c_1$ ). This "pivotal point" was found for all five streams investigated. The pivotal point was found to generally be at a very low flow (high concentration). An explanation for this behavior may be that there is some small flow rate at which not only all of the flow comes from groundwater sources, but that the groundwater has sufficient retention time

to reach saturation equilibrium with the surrounding source materials. There is a small periodic variation in the pivotal point in the form of the  $d_{\tau}$  term, attributable to temperature variation, evaporation and similar secondary effects. The value of  $d_{\tau}$  is expected to be positive for periods of high temperature and evaporation and negative for periods of low temperature and evaporation. Different results may be produced without contradiction of this explanation because of errors in the estimation of the harmonic slope term. The pivotal point concept results in a slightly more complex equation to fit than Equation 5-34 to which it reduces. It has the advantage of reducing the number of harmonics needed. In some cases the periodic correction term  $d_{\tau}$  can be neglected. In any event the linear relationship between  $a_{\tau}$  and  $b_{\tau}$  accounts for most of the variance of the intercept so that it may be replaced by  $c_1$ ,  $c_2$  and the small periodic term  $d_{\tau}$ .

In order to fit Equations 5-34 and 5-36, the following procedure is taken. The basic equation, Equation 5-29, is fitted to data from intervals within the year. A weighted linear regression between the slope and intercept terms provides the values of  $c_1$  and  $c_2$ . Weights used are the inverse of the variance estimates for the individual slopes. The same weights are also used to perform a weighted harmonic analysis for the slope term. Once the individual values for the slope term have been fit by a periodic function, and  $c_1$  and  $c_2$  have been estimated, new values for the individual  $b_{\tau}$  and  $d_{\tau}$  terms are re-estimated by insuring that the individual relationships using the fitted slopes pass through the logarithmic mean values for the flow and conductivity. The individual values for the  $b_{\tau}$  and  $d_{\tau}$  terms are then fit by ordinary Fourier analysis techniques.

### 5.7 Antecedent Flow Correlations

An attempt is made to correlate the residuals from the application of Equation 5-36 to antecedent flow conditions. The primary objective is to determine if the residuals are correlated with increments in discharge. The residual series is cross correlated with a series  $D_i$  given by

$$D_i = \log Q_i - \log Q_{i-1} \quad (5-37)$$

$D_i$  can be interpreted as a variable indicating the rate and direction of changes in discharge. Study on all five streams shows that small though significant correlations are found for the Henry's Fork, Saline and Pecos Rivers. These correlations, however, are not high, accounting for less than two percent of the total variance. Since these correlations explain only a small portion of the total variance for three of the five streams while insignificant on the others, this correlation analysis of residuals is rejected as a method for explaining the antecedent effects.

In a further attempt to determine the effect of antecedent conditions, particularly in the form of a hysteresis effect, conductivity and flow values were related graphically using consecutive daily values. No differences in the behavior of the conductivity

were found between the rising and falling limbs of the hydrograph during flood events.

### 5.8 Results of Time Lag Analysis

In analyzing the data to determine if any time lag exists in the relationship between flow and conductivity, a cross correlation analysis was performed for each stream with lags from -50 to +50 (positive lag indicating conductivity leading flow). The results of this analysis lead to the conclusion that there is no significant improvement by considering the lagged relationship.

As indicated in Table 5-3, a higher correlation was found by correlating the flow values at Crowheart rather than flow values at Riverton with the conductivities measured at Riverton. Although this result indicates the use of Crowheart flow data is advantageous, the relationship using Riverton flow data is generally much stronger when the data are further examined on a monthly basis. The apparent conclusion is that a comparison of this type should not be made without accounting for the periodic variation. For the remainder of this study no further use of the flow data at Crowheart will be made.

Table 5-3. Results of Cross Correlation Analysis.

$R^2$ for Zero Lag	Stream	Maximum $R^2$	Lag
0.72	Henry's Fork River (1950-1959)	0.73	1
0.60	New Fork River	0.61	-3
0.83	Pecos River	0.83	0
0.84	Saline River	0.84	0
0.72	Wind River		
	Crowheart	0.73	1
0.54	Riverton	0.54	0

### 5.9 Split Sample Results

As mentioned previously, the Henry's Fork River, for which 22 years of daily data are available, was chosen for use in a detailed test of the selected equations. The sample is split into three parts: (1) the first ten years are used to estimate the parameters for the equations; (2) the next ten years of data are used to verify the use of the equations and accuracy of the parameters; and (3) the last two years of data are reserved for later use in predicting and simulating both conductivity and ion concentrations as described in Chapters 9 and 10. The results are shown in Tables 5-4 and 5-5, where  $R^2$  is the square of the correlation coefficient, or the decimal fraction of explained variance, and  $\sigma^*$  is the standard deviation of differences between the estimated and observed values for the log conductivity. The  $R^2$  and  $\sigma^*$  values shown are given in terms of the logarithms of the conductivity.

Both the  $R^2$  and  $\sigma^*$  values are important and neither one of them alone is sufficient to judge the results of the fit.  $R^2$  is a measure of the strength of the relationship and  $\sigma^*$  is an indication of what remains unexplained after the fit. A low value of  $R^2$  is not serious if it is accompanied by a low value of  $\sigma^*$ . On the other hand, a high value of  $R^2$  indicates

Table 5-4. Fit of parameters to the Henry's Fork River data for the period 1950-1959.

Equation 5-29	$\log \kappa = a \log Q + b$ $a = -0.184$ $b = 3.39$
Equation 5-31	$\log \kappa = a \log Q + b_\tau$ $a = -0.184$ Number of harmonics in $b_\tau = 7$
Equation 5-33	$\log \kappa = a_w \log Q + b_\tau$ $a_w = -0.176$ Number of harmonics in $b_\tau = 7$
Equation 5-34	$\log \kappa = a_\tau \log Q + b_\tau$ Number of harmonics in $a_\tau = 2$ Number of harmonics in $b_\tau = 2$
Equation 5-35	$b_\tau = c_2 - c_1 a_\tau$ $c_1 = 1.05$ $c_2 = 3.21$ $R_2 = 0.83$ $\sigma^* = 0.032$
Equation 5-36	$\log \kappa = a_\tau (\log Q - c_1) + c_2 + d_\tau$ Number of harmonics in $a_\tau = 2$ Number of harmonics in $d_\tau = 2$

Table 5-5. Results of applications to the Henry's Fork River data using parameter values given in Table 5-4.

Equation:	<u>5-29</u>	<u>5-31</u>	<u>5-33</u>	<u>5-34</u>	<u>5-36</u>
<u>Henry's Fork, 1950-1959</u>					
$R^2$	0.72	0.80	0.80	0.82	0.82
$\sigma^*$	0.089	0.075	0.074	0.070	0.070
<u>Henry's Fork, 1960-1969</u>					
$R^2$	0.62	0.73	0.73	0.72	0.72
$\sigma^*$	0.086	0.073	0.073	0.073	0.074

a great deal of explained variance using the relationship regardless of the value of  $\sigma^*$ . In examining the results, it is advantageous to remember that an error of 0.01 in the logarithm (base 10) is approximately 2.3 percent in the value (i.e., for small x,  $e^x \approx 1+x$ ). As shown by the results of Table 5-5, the standard deviations of the residuals are approximately the same for both the data used for parameter estimation and the later data used for model verification. The  $R^2$  values however are lower, reflecting less total fluctuation in the later data. In this particular application, no advantage is apparent in using the weighted slope of Equation 5-33 over the unweighted slope of equation 5-31 when using a periodic intercept.

In using a periodic slope on the split sample data the number of significant harmonics in  $b_\tau$  and  $d_\tau$  were reduced as shown in Table 5-5. This advantage is tempered by the fact that very little improvement is accomplished by the addition of a periodic slope. The use of the pivotal point does not significantly improve the relationship but it did result in a lower variance of  $d_\tau$  than was found for  $b_\tau$ .

The general conclusion reached in this analysis is that all the equations are applicable and that a periodic term is justified. The standard deviation of the residuals are approximately the same regardless of whether the data are used in estimating the parameters or not. Equation 5-36 appears to be slightly favorable over the others because the slope term and the  $d_\tau$  term are linearly independent and because the relationship more closely approximates the observed fits made using small time intervals.

The effects of using various intervals for fitting the equations was studied. It was found that 73 intervals in the year, or five-day intervals, gave satisfactory estimates for the periodic terms.

### 5.10 Results of Application to All Data

A simple linear logarithmic relationship, Table 5-6, explains a large portion of the variance in the log conductivity for all of the streams. The values of  $R^2$  and  $\sigma^*$  shown in the table (and subsequent tables of this section) are in terms of the logarithms of the conductivity and as a result are dimensionless. The explained variance in  $\log \kappa$  varied from 54 to 84 for the five streams using the simple linear logarithmic relationship. The units for conductivity are taken as micromhos per centimeter and the units for discharge are taken as cubic feet per second.

Table 5-6. Fit of Equation 5-29.

$$\log \kappa = a \log Q + b$$

Stream	a	b	R <sup>2</sup>	σ*
Henry's Fork River	-0.189	3.39	0.69	0.088
New Fork River	-0.308	3.08	0.60	0.097
Pecos River	-0.561	4.52	0.83	0.066
Saline River	-0.492	4.21	0.84	0.116
Wind River				
Crowheart	-0.327	3.54	0.72	0.074
Riverton	-0.280	3.33	0.54	0.096

As shown in Tables 5-7 and 5-8 the addition of a periodic intercept term greatly improves the fit. In Tables 5-7 the slope term is taken as that given by the fitting of the simple linear equation, Equation 5-29, while in Table 5-8 the slope term is a weighted value obtained by a procedure described in Section 5.6. The use of weighted estimates for the slope gives negligible improvement over the unweighted approach. As an example, estimated and fitted values of  $b_\tau$  for the New Fort River data are shown in Figures 5-9 and 5-10 for the unweighted and weighted approaches respectively. In both cases the annual variation in  $b_\tau$

shows essentially the same behavior. The explained variance in  $\log \kappa$  for this case ranges from 76 to 86 percent.

Table 5-7. Fit of Equation 5-31.

$$\log \kappa = a \log Q + b_\tau$$

Stream	Number of Harmonics		R <sup>2</sup>	σ*
	a	in $b_\tau$		
Henry's Fork River	-0.189	1	0.76	0.077
New Fork River	-0.308	4	0.81	0.067
Pecos River	-0.561	1	0.84	0.063
Saline River	-0.492	3	0.84	0.115
Wind River	-0.280	2	0.80	0.063

Table 5-8. Fit of Equation 5-33.

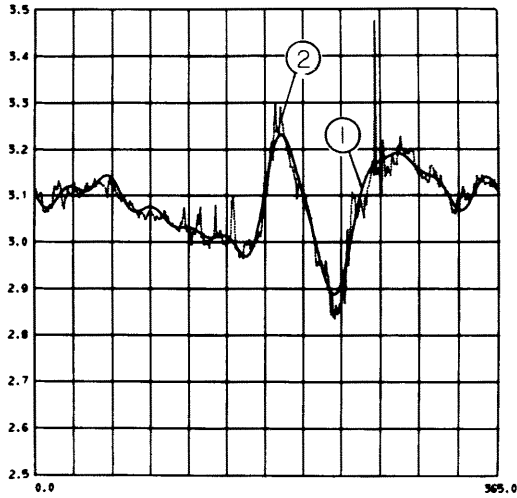
$$\log \kappa = a_w \log Q + b_\tau$$

Stream	a <sub>w</sub>	Number of Harmonics		R <sup>2</sup>	σ*
		in $b_\tau$			
Henry's Fork River	-0.179	1		0.76	0.077
New Fork River	-0.459	4		0.80	0.068
Pecos River	-0.468	2		0.86	0.061
Saline River	-0.475	3		0.84	0.115
Wind River	-0.256	2		0.81	0.062

By utilizing both a periodic slope and a periodic intercept, additional improvement is observed with the explained variance in  $\log \kappa$  ranging from 81 to 87 percent for the five streams. The number of harmonics used and the measures of goodness of fit are shown in Table 5-9. As an example of the observed annual variation in the periodic slope and intercept, Figures 5-11 and 5-12 give the observed and fitted values for the Wind River data. As can be readily observed from the two figures, there is a strong negative correlation between the slope and intercept values. Similar results were obtained using the data from the other four streams.

As shown in Table 5-10 the slope and intercept values when fitted using small intervals in the year show a high linear correlation on all of the streams. Figure 5-13 shows this relation for the Wind River. By making use of this property, there is a substantial reduction in the variance of the periodic intercept  $d_\tau$ , as used in Equation 5-36, compared with  $b_\tau$  as used in Equation 5-34. The values  $R_w^2$  and  $\sigma_w^*$  refer to the decimal percent explained variance in the weighted values and the standard deviation of the weighted residuals. A more complete description of these terms and their method of calculation is given in Chapter 8. A comparison of the variances of the estimates for  $b_\tau$  and  $d_\tau$  is given in Table 5-11.

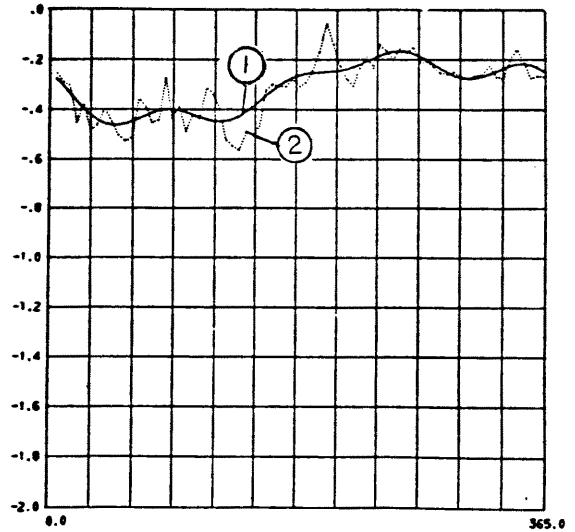
Periodic Intercept,  $b_T$



Time of Year, year beginning October 1.

Figure 5-9. Harmonic fit of  $b_T$  of Equation 5-31 for the New Fork River data: (1) fitted; (2) observed.

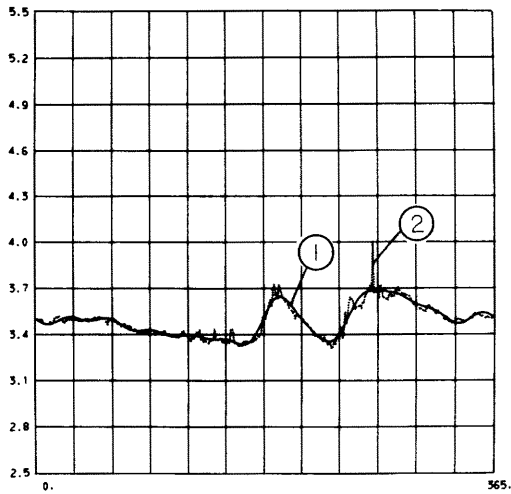
Periodic Slope,  $a_T$



Time of Year

Figure 5-11. Harmonic fit of  $a_T$  of Equation 5-34 for the Wind River data: (1) fitted; (2) observed.

Periodic Intercept,  $b_T$



Time of Year, year beginning October 1.

Figure 5-10. Harmonic fit of  $b_T$  of Equation 5-33 for the New Fork River data: (1) fitted; (2) observed.

Table 5-9. Fit of Equation 5-34

Stream	Number of Harmonics in $a_T$	Number of Harmonics in $b_T$	$R^2$	$\sigma^*$
Henry's Fork River	2	4	0.81	0.070
New Fork River	6	8	0.86	0.056
Pecos River	3	3	0.87	0.058
Saline River	4	4	0.85	0.113
Wind River	4	5	0.84	0.057

Table 5-10. Fit of Equation 5-35.

Stream	$c_1$	$c_2$	$R_w^2$	$\sigma_w^2$
Henry's Fork River	1.03	3.19	0.72	0.027
New Fork River	2.28	2.42	0.95	0.054
Pecos River	1.97	3.39	0.99	0.033
Saline River	1.37	3.54	0.87	0.030
Wind River	3.39	2.29	0.89	0.058

Periodic Intercept,  $b_T$

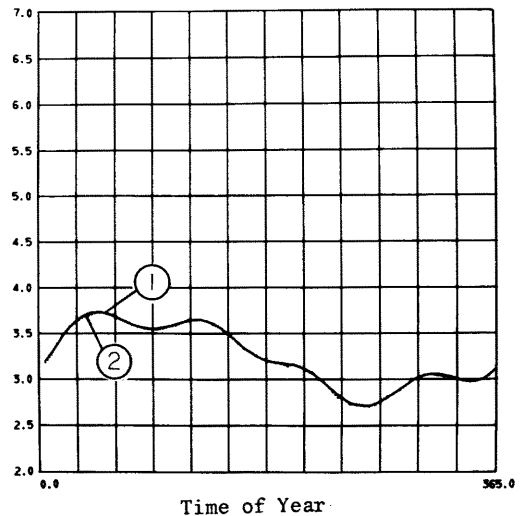
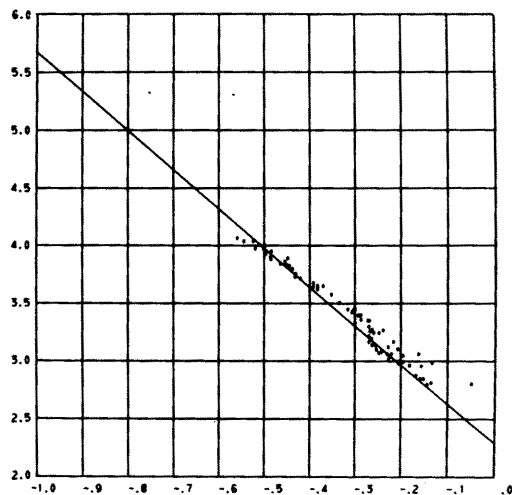


Figure 5-12. Harmonic fit of  $b_T$  of Equation 5-34 for the Wind River data: (1) fitted; (2) observed.

Table 5-11. Comparison of variances of estimates of  $b_\tau$  and  $d_\tau$ .

Stream	$b_\tau$ and $d_\tau$	
	Variance of $b_\tau$	Variance of $d_\tau$
Henry's Fork River	0.0033	0.0011
New Fork River	0.0921	0.0084
Pecos River	0.1545	0.0012
Saline River	0.0044	0.0010
Wind River	0.1017	0.0034

Intercept Values,  $b_\tau$



Slope Values,  $a_\tau$

Figure 5-13. Estimates of the periodic intercept,  $b_\tau$ , versus estimates of the periodic slope,  $a_\tau$ , for the Wind River data.

The values of  $c_1$  and  $c_2$  seem to agree with the explanation of the pivotal point with the exception of the Wind River. This deviation may be the result of irrigation within the basin, or there may be a different governing process. For the other four streams, the values of  $c_1$  correspond to very low flows while the values of  $c_2$  correspond to high conductivities, as expected.

Equation 5-36 was applied to all five streams and the results are shown in Table 5-12. Since this equation is basically the same equation as Equation 5-34, the fit is essentially the same. However, in this case, the number of significant harmonics for the variance of the intercept term is greatly reduced for all of the streams. Figure 5-14 illustrates the annual variation in  $d_\tau$  noted for the Wind River data.

Table 5-12. Fit of Equation 5-36.

$$\log \kappa = a_\tau (\log Q - c_1) + c_2 + d_\tau$$

Stream	Number of Harmonics in $a_\tau$	Number of Harmonics in $d_\tau$	$R^2$	$\sigma^*$
Henry's Fork River	2	4	0.81	0.070
New Fork River	6	5	0.85	0.059
Pecos River	3	2	0.87	0.059
Saline River	4	1	0.84	0.114
Wind River	4	5	0.84	0.057

Note: Values of  $c_1$  and  $c_2$  used are contained in Table 5-10.

Periodic Intercept,  $d_\tau$

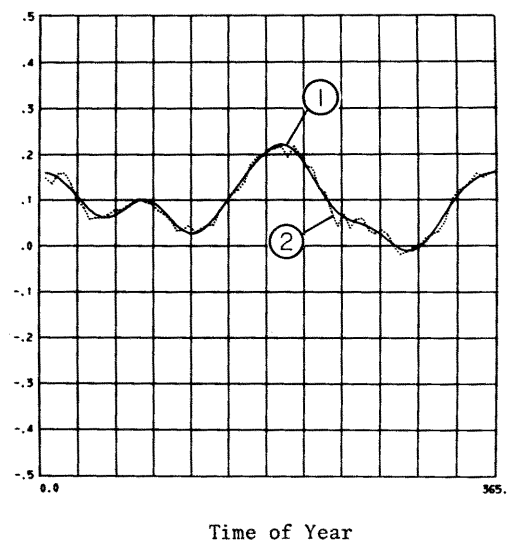


Figure 5-14. Harmonic fit of  $d_\tau$  of Equation 5-36 for the Wind River data: (1) fitted; (2) observed.

### 5.11 Analysis of Residuals

The residuals  $\epsilon$  resulting from the fit by Equation 5-36 were examined for autoregressive dependence, where  $\epsilon$  is computed from

$$\log \kappa = a_\tau (\log Q - c_1) + c_2 + d_\tau + \epsilon. \quad (5-38)$$

The correlograms of  $\epsilon$  for each stream and for the first six lags only are given in Table 5-13.

The series of residuals are highly autocorrelated, with a great deal of persistence. Both the first and second-order autoregressive models are examined. On four of the five streams, very little improvement over the first-order model is found by using the second-order model, so the first-order model is selected.

Table 5-13. Autocorrelation coefficients.

Stream	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>	r <sub>5</sub>	r <sub>6</sub>
Henry's Fork River	0.76	0.63	0.58	0.52	0.49	0.47
New Fork River	0.58	0.51	0.44	0.39	0.39	0.29
Pecos River	0.35	0.07	0.13	0.14	0.13	0.15
Saline River	0.65	0.50	0.42	0.37	0.35	0.34
Wind River	0.74	0.64	0.56	0.50	0.47	0.44

However, for the New Fork River the second-order model is found to be significant and is selected. The method for estimating the model coefficients and for determining the explained variance are described in Chapter 8.

Given the value of the first residual, the subsequent values are obtained by

$$\epsilon_i = a_1 \epsilon_{i-1} + \xi_i, \quad (5-39)$$

for the first-order autoregressive model. Given the values of the first two residuals, the subsequent values are obtained by

$$\epsilon_i = a_1 \epsilon_{i-1} + a_2 \epsilon_{i-2} + \xi_i, \quad (5-40)$$

for the second-order autoregressive model.  $\xi$  is considered to be a linearly independent stochastic component. For this study, the distribution of the independent stochastic component is taken to be normal with a mean zero and a standard deviation as given in Table 5-14.

Table 5-14. Autoregressive coefficients.

Stream	a <sub>1</sub>	a <sub>2</sub>	Standard Deviation of $\xi$
Henry's Fork River	0.76		0.046
New Fork River	0.43	0.26	0.046
Pecos River	0.35		0.052
Saline River	0.65		0.066
Wind River	0.74		0.026

### 5.12 Fitted and Observed Conductivity Series

Using Equation 5-36, the fitted values for conductivity were generated using the discharge series. The resulting fitted conductivity along with the observed values are plotted for one year for each of the five streams in Figures 5-15 through 5-19. Agreement is quite good, with deviations generally less than 15 percent. As shown in Table 5-12, the standard deviation of the residual ranges from 0.057 to 0.114, which corresponds to approximately 15 to 30 percent deviations. Much of the standard deviation of residuals can be attributed to a limited number of points in the series, some of which may have some gross errors. For example, a recorded conductivity may be given as 1600  $\mu\text{U}/\text{cm}$  while it appears more likely to

Conductivity,  $\mu\text{U}/\text{cm}$

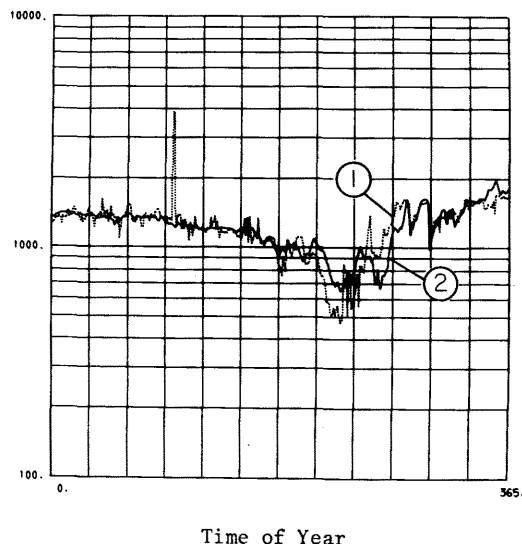


Figure 5-15. Measured (1) and fitted (2) conductivity of the Henry's Fort River for the water year beginning October 1, 1968.

be 160  $\mu\text{U}/\text{cm}$ . Two examples of questionable data points are shown in Figures 5-15 and 5-16. One is in the month of January of the Henry's Fork River, Figure 5-15, and the other is in the month of June of the New Fork River, Figure 5-16. Errors in recording, misplaced decimals or transposed digits, while quite rare, may account for a portion of the unexplained variance. These mistaken points quite likely prevent the accurate estimation of equation parameters and harmonic terms.

## WASHINGTON WATER

### 5.15 Closing Remarks **RESEARCH CENTER LIBRARY**

It was found that a basic linear relation between the logarithms of flow and conductivity explains from 54 to 84 percent of the variance of the logarithms of the conductivity. The addition of a periodic intercept significantly improves the relationship. The explained variance in this case ranged from 76 to 86 percent, with the standard deviation of residuals, in terms of the log of conductivity, ranging from 0.061 to 0.115. The use of a weighted slope was not found to be justified.

The use of both a periodic slope and a periodic intercept improves the relation somewhat, increasing the explained variance to between 81 and 87 percent, although a larger number of harmonics is needed. The periodic slope and the periodic intercept were found to be highly correlated. As a result of this correlation, a pivotal point concept is hypothesized. On all five streams, it was found that regardless of the time of year the discharge-conductivity relationship always passed through a common discharge-conductivity point. This pivotal point may be explained as being at a low flow where all flow originates from groundwater sources and where the retention time is sufficient to achieve a saturated concentration with respect to the surrounding source materials. This concept was verified

Conductivity,  $\mu\text{U}/\text{cm}$

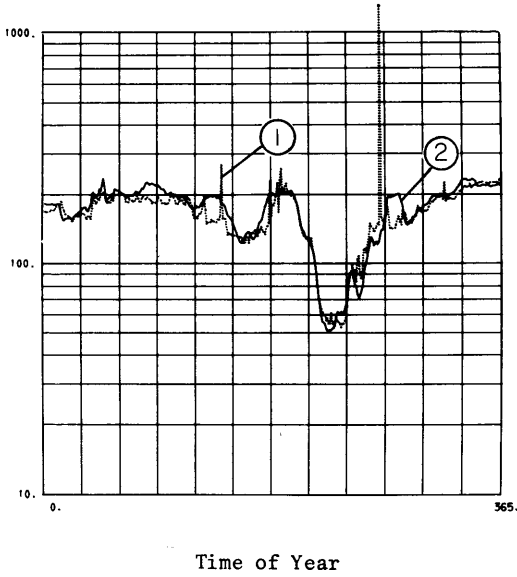


Figure 5-16. Measured (1) and fitted (2) conductivity of the New Fork River for the water year beginning October 1, 1968.

Conductivity,  $\mu\text{U}/\text{cm}$

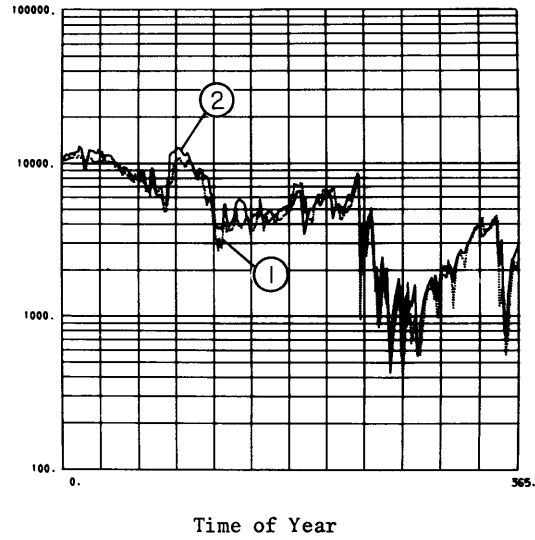


Figure 5-18. Measured (1) and fitted (2) conductivity of the Saline River for the water year beginning October 1, 1966.

Conductivity,  $\mu\text{U}/\text{cm}$

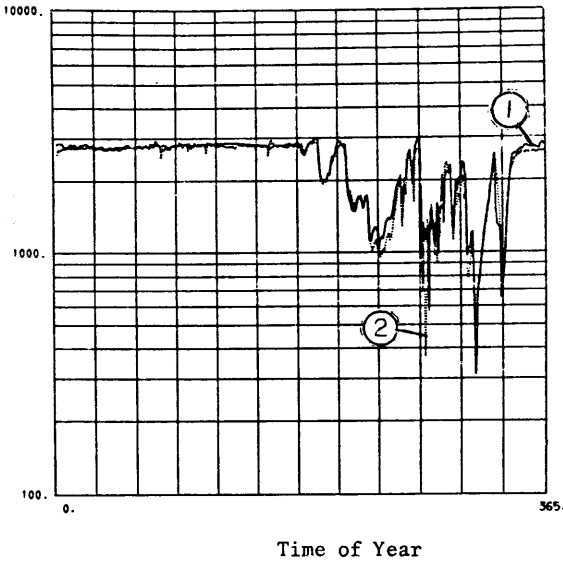


Figure 5-17. Measured (1) and fitted (2) conductivity of the Pecos River for the water year beginning October 1, 1967.

Conductivity,  $\mu\text{U}/\text{cm}$

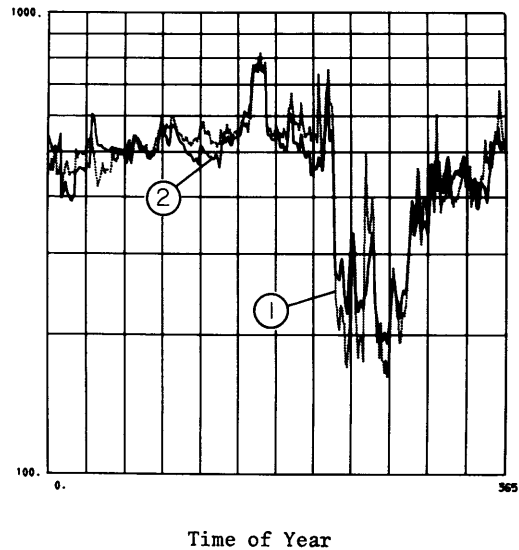


Figure 5-19. Measured (1) and fitted (2) conductivity of the Wind River for the water year beginning October 1, 1969.

by the data. The pivotal point was found to be at a very low flow for four of the streams and a fairly low flow for the fifth. This pivotal point concept was further discussed in Section 5.6 of this chapter.

The easiest relationship which gives reasonably good results in Equation 5-31 with an unweighted slope and a periodic intercept. For cases where the data available for the estimation of parameters is very

limited, the use of this relationship is practical. For cases where more data is available or where a more accurate relationship is desired and justified, the use of both a periodic slope and a periodic intercept is recommended. Equation 5-34 is the basic relationship possessing both a periodic slope and a periodic intercept, however Equation 5-36 is preferable. This equation is an improved form of Equation 5-34, obtained by removing the dependence between the periodic slope

and periodic intercept. This equation will be used in all subsequent calculations.

The results of this investigation show that the relationships used are potentially applicable to natural streams in general. The fact that the relationships appear to be generally applicable is of considerable importance. The methods were arrived at using daily data. The use of daily data represents a significant improvement over the use of weekly or monthly data as has been commonly done in the past. By considering conductivity measurements as indications of the total salt concentration, the usefulness of the conductivity measurements is greatly increased. In Chapter 7 the relationship between conductivity and the constituents found in solution will be examined and applied. The use of periodic terms, estimated by Fourier analysis, represents an improved objective approach to the treatment of annual variations in the discharge-conductivity relationship. An interesting discovery which may later prove to be of importance is the observation of a pivotal point. In the future, if studies using other streams support this finding, a more complete knowledge of the discharge-quality relationship may be gained by further investigation of the pivotal point concept.

In future application of the methods used here, it is recommended that Equation 5-36 be adopted. The procedure for fitting this relation is as follows:

1. Divide the available data into a number of intervals within the year. In this study 73 five day intervals were found to work well.

2. Fit a linear logarithmic relation to the data from each interval separately. This results in as many joint estimates for the slope and intercept as there are intervals.

3. Using Fourier analysis techniques, fit harmonics to the estimated values for the slope. As a matter of practicality, rather than taking only the significant harmonics, the first six harmonics could be accepted and would be adequate.

4. The values of  $c_1$  and  $c_2$  are obtained by a linear regression between the slope estimates and the intercept estimates.

5. Using the fitted values for the periodic slope  $a_\tau$  and the values of  $c_1$  and  $c_2$ , an estimate for  $d_\tau$  is obtained for each of the intervals by requiring the relationship to pass through the mean values for the  $\log \kappa$  and  $\log Q$ .

6. The estimates for  $d_\tau$  are fit by harmonics using Fourier analysis. The use of the first six harmonics is generally adequate.

Once the relationship has been fit to the data in this manner, it may be used to predict the conductivity time series given the discharge time series. It would be expected that the errors of prediction would be of approximately the same magnitude as the errors involved in the fit of the data used in estimating the parameters.



## Chapter 6 MODELS FOR ION PROPORTIONS

This chapter deals with the models used to relate the proportions of the various ions to hydrologic variables. The procedure followed is similar to that used in relating conductivity to discharge and time of year: a priori expected relationships are discussed and then basic equations are selected.

The approach of studying the relationships using ion or constituent proportions rather than constituent concentrations is somewhat unique. This approach allows for an efficient use of the available data. The limited amount of chemical analysis data often available is not as critical when relating the constituent proportions to discharge as when relating constituent concentrations to discharge since the variability of the proportions is much less than that of the concentration.

### 6.1 Definition of Terms

The proportion of a constituent is defined in this study as the ratio of its concentration to the total salt concentration. The concentrations are expressed as equivalents per liter. Some slight modifications are made in the application of this definition to actual data. Proportions of cations are calculated as the ratio of the ion concentration to the total cation concentration. In a similar manner, proportions of anions are calculated. For nonionic species, proportions are calculated as the ratio of the particular constituent's moles per liter concentration to the equivalents per liter of cations plus the equivalents per liter of anions. For simplicity all of the proportions will at times be referred to as "ion proportions." To insure that the chemical analyses used are complete and accurate, only those analyses are used which included the determination of the major ions (calcium, magnesium, sodium, potassium, bicarbonate, sulfate and chloride) while also meeting the charge balance recommendations of the American Public Health Association et al. (1965) for the accuracy of analysis. It should be noted that the proportions used are those calculated from the recorded results of chemical analyses. For example, the sulfate proportion is the proportion of total sulfate in all forms to the total concentration of anions in all forms. The total concentration in this case is not in reality the total concentration of the actual anions in solution, but that concentration assuming no complex formation. Likewise, the use of the total sulfate is not the same as using the free sulfate ion concentration. As an example, for the data of Table A4-6, the total ion concentration is reduced from 19.7 to 15.8 meq/l and the sulfate concentration is reduced from 14.1 to 10.4 meq/l by accounting for ion associations. Although analytic proportions used here are not "true" ion proportions, they are preferable to the actual ion proportions. The total sulfate, chloride and other concentrations are commonly determined by chemical analysis and are of interest since they completely define the solution. The actual free ion concentrations, however, are only a result of chemical equilibria within the solution and can be calculated using equilibrium constants for the chemical equilibria involved.

### 6.2 A Priori Expectations

Since the total concentration of salts is found to be related to discharge by a linear logarithmic equation it would also be expected that the individual ions would also have the same form of relationship.

Using the basic relationship

$$\log C_T = a \log Q + b \quad (6-1)$$

for the total salt concentration, and

$$\log C_i = a_i \log Q + b_i \quad (6-2)$$

for the individual ions, the ion proportions are then given by

$$\log P_i = \log C_i - \log C_T = (a_i - a) \log Q + b_i - b \quad (6-3)$$

Thus the expected basic relationship for the ion proportions would be a linear logarithmic relation with flow.

A more complicated idealistic model could also be developed along parallel lines to that done for the conductivity in Chapter 5.

The use of composite samples for the chemical analyses is not expected to adversely affect the results. The composition procedure is done with daily samples which are considered to be of the same nature, that is, they have similar conductivity and similar flow conditions at the same time of the year. However, these recommendations for the composition of samples are not always followed. For cases where the conductivity and flow conditions vary widely among the daily samples making up the composite, the effect could be serious. For the streams studied, the errors due to composition are felt to be minor.

### 6.3 Selection of Ion Proportion Models

In plotting the actual data, it is apparent that the variation in discharge explains much of the variation in ion proportions. It should be emphasized that ion proportions were found to be relatively constant on all streams except for the Saline River. For the Saline River, the ions were found to vary widely, but in a distinct relation to discharge. For the other four streams proportions of many of the ions showed only small variations. Three basic equations were found to be applicable:

$$\text{logarithmic,} \quad \log P_i = a_i \log Q + b_i ; \quad (6-4)$$

$$\text{semilogarithmic,} \quad P_i = a_i \log Q + b_i ; \quad (6-5)$$

$$\text{and constant,} \quad P_i = a_i \quad (6-6)$$

Figures 6-1, 6-2 and 6-3 illustrate each of the three relationships.

Proportions

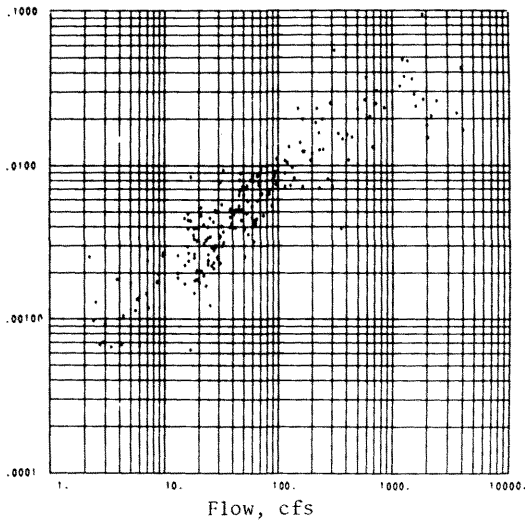


Figure 6-1. Observed bicarbonate ion proportions versus flow for the Saline River. Logarithmic relationship.

Proportions

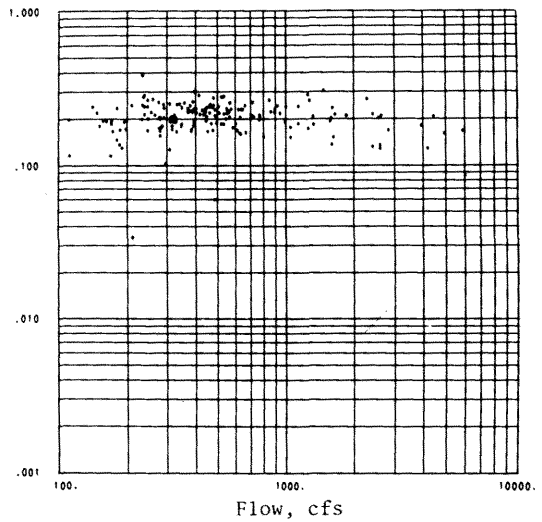


Figure 6-3. Observed magnesium ion proportions versus flow for the Wind River. Constant relationship.

Proportions

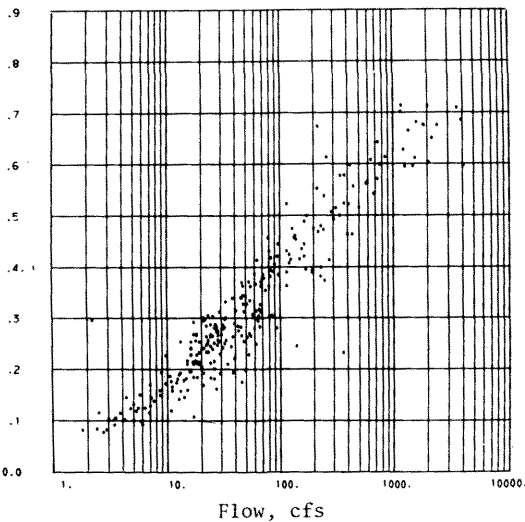


Figure 6-2. Observed calcium ion proportions versus flow for the Saline River. Semilogarithmic relationship.

In selecting the model to use for the relation of a particular ion with discharge, the following procedure was followed. The parameters of the logarithmic and semilogarithmic models were estimated. Both models were then used to predict the ion proportions and to calculate the coefficient of determination,  $R^2$ . The  $R^2$  value for the logarithmic relation  $R_1^2$ , and the  $R^2$  value for the semilogarithmic relation  $R_S^2$  are both calculated in terms of the proportions. This means that the  $R_1^2$  was determined for the untransformed proportions, not for the logarithms of the proportions, so that  $R_1^2$  and  $R_S^2$  could be compared on a common basis. Usually the model having the highest  $R^2$  was chosen. However, the logarithmic relation was given preference since it is consistent with the basic relation found between total concentration and discharge.

This aspect was discussed in Section 6.2 of this Chapter. In cases of low or insignificant  $R^2$  values, the constant relation was considered. A visual examination of the plotted data aided the selection of the ion proportion models.

Generally the logarithmic and constant relations sufficed. However, for the Saline River, the proportions for three of the major ions were definitely better fit by the semilogarithmic relation of Equation 6-5. For the majority of the ions the choice between the logarithmic and semilogarithmic relations is not apparent. The proportions of the ions do not vary greatly and the fit by the two relations gives similar results. The fit by the logarithmic relation of Equation 6-4 is usually better, and this relation is generally chosen.

Ion proportions were also plotted against time of year. For this plotting, time of year was selected as the average of the dates of the first and last daily samples which made up the composite sample. No relation was found between the ion proportions and time of year.

#### 6.4 Application of Models

The model was applied for each of the thirteen ions for each of the five streams. Table 6-1 gives the results. This table lists the  $R^2$  values for both the logarithmic and semilogarithmic relations and the model selected for each of the ions. As expected the explained variances are generally small. This is mainly due to the fact that the proportions do not vary greatly from being constants. An exception to this are the major ions for the Saline River data which do vary considerably and accordingly the corresponding relationships show high explained variances.

Table 6-2 gives the parameters of the selected relationships along with the residual standard deviations. In applying the models to various ions, an important factor is the variance or standard deviation of residuals. It should be noted that the standard deviations of residuals  $\sigma^*$  are in terms of the fitted relationship. That is,  $\sigma^*$  is in terms of the

proportions for the semilogarithmic and constant relationships and in terms of the logarithms for the logarithmic relationship. The values of a and b shown are the values of the regression coefficients

for either Equation 6-4, 6-5, or 6-6 depending on whether the relationship is logarithmic, semilogarithmic or constant, respectively. Since the proportions are dimensionless, neither the values for the means or  $\sigma^*$  have any units.

Table 6-1. Application of models to ion proportions.

Stream	Henry's Fork			New Fork			Pecos			Saline			Wind		
Ion	$R_1^2$	$R_S^2$	M	$R_1^2$	$R_S^2$	M	$R_1^2$	$R_S^2$	M	$R_1^2$	$R_S^2$	M	$R_1^2$	$R_S^2$	M
Calcium	0.38	0.36	L	0	0	C	0.02	0.02	C	0.77	0.88	S	0.33	0.32	L
Magnesium	0.11	0.10	L	0	0	C	0.12	0.13	C	0.07	0.07	C	0	0	C
Sodium	0.35	0.35	L	0.04	0.04	C	0	0	C	0.73	0.89	S	0.46	0.44	L
Potassium	0.39	0.35	L	0.30	0.19	L	0.59	0.67	S	0.63	0.59	L	0.33	0.31	L
Iron	0.06	0.03	L	0.48	0.27	L	0.47	0	L	0.37	0.22	L	0.23	0.12	L
Hydrogen Ion	0.33	0.26	L	0.5	0.08	L	0.36	0.44	L	0.57	0.48	L	0.24	0.23	L
Bicarbonate	0.75	0.68	L	0	0	C	0.94	0.95	L	0.80	0.79	L	0.51	0.50	L
Sulfate	0.59	0.65	S	0	0	C	0.91	0.92	L	0.09	0.10	C	0.46	0.47	L
Chloride	0.14	0.13	L	0.02	0	C	0.17	0.18	L	0.69	0.86	S	0.05	0.05	L
Fluoride	0.44	0.31	L	0.21	0.17	L	0.44	0.44	L	0.71	0.66	L	0.02	0.02	C
Nitrate	0.08	0.05	C	0.05	0.04	L	0	0.36	S	0	0.45	S	0.13	0.11	C
Boron	0	0	C	0.18	0.12	L	0.33	0.37	L	0.23	0.17	L	0.03	0.04	L
Silica	0.49	0.42	L	0.33	0.31	L	0.95	0.92	L	0.50	0.55	L	0.58	0.60	L

$R_1^2$  indicates  $R^2$  for the logarithmic relationship, Equation 6-4.

$R_S^2$  indicates  $R^2$  for the semilogarithmic relationship, Equation 6-5.

M indicates model selected where S = Semilogarithmic, L = Logarithmic and C = Constant.

Table 6-2. Selected ion proportion relationships to discharge.

Henry's Fork River					
Ion	Mean	Relationship	a	b	$\sigma^*$
Calcium	0.47	Log	0.037	-0.39	0.03
Magnesium	0.35	Log	-0.022	-0.42	0.06
Sodium	0.16	Log	-0.060	-0.69	0.06
Potassium	0.016	Log	0.092	-1.95	0.08
Iron	$2.2 \times 10^{-4}$	Log	0.320	-4.50	0.45
Hydrogen	$8.5 \times 10^{-7}$	Log	0.241	-6.60	0.29
Bicarbonate	0.31	Log	0.163	-0.78	0.07
Sulfate	0.64	Semilog	-0.101	0.80	0.06
Chloride	0.044	Log	-0.041	-1.30	0.08
Fluoride	0.0024	Log	0.207	-3.04	0.17
Nitrate	0.0011	Constant	0.0011		0.0015
Boron	$6.8 \times 10^{-4}$	Constant	$6.87 \times 10^{-4}$		$2.1 \times 10^{-4}$
Silica	0.013	Log	0.140	-2.14	0.11

Table 6-2 (Contd.). Selected ion proportion relationships to discharge.

<u>New Fork River</u>					
<u>Ion</u>	<u>Mean</u>	<u>Relationship</u>	<u>a</u>	<u>b</u>	<u><math>\sigma^*</math></u>
Calcium	0.60	Constant	0.602		0.06
Magnesium	0.19	Constant	0.186		0.06
Sodium	0.19	Constant	0.188		0.03
Potassium	0.023	Log	0.170	-2.13	0.16
Iron	0.0019	Log	0.532	-4.27	0.32
Hydrogen	$7.6 \times 10^{-4}$	Log	0.917	-7.46	0.51
Bicarbonate	0.82	Constant	0.816		0.06
Sulfate	0.13	Constant	0.134		0.06
Chloride	0.041	Constant	0.041		0.02
Fluoride	0.0062	Log	0.161	-2.66	0.13
Nitrate	0.0023	Log	0.255	-3.38	0.33
Boron	$8.0 \times 10^{-4}$	Log	0.337	-4.07	0.26
Silica	0.041	Log	0.148	-1.81	0.09

<u>Pecos River</u>					
<u>Ion</u>	<u>Mean</u>	<u>Relationship</u>	<u>a</u>	<u>b</u>	<u><math>\sigma^*</math></u>
Calcium	0.75	Constant	0.746		0.02
Magnesium	0.15	Constant	0.145		0.01
Sodium	0.11	Constant	0.105		0.01
Potassium	0.0027	Semilog	$5.56 \times 10^{-3}$	$-8.79 \times 10^{-3}$	$1.2 \times 10^{-3}$
Iron	$2.2 \times 10^{-5}$	Log	0.404	-5.43	0.16
Hydrogen	$5.7 \times 10^{-7}$	Log	1.023	-8.65	0.26
Bicarbonate	0.097	Log	0.647	-2.41	0.04
Sulfate	0.81	Log	-0.100	0.11	0.01
Chloride	0.094	Log	-0.100	-0.83	0.07
Fluoride	0.0012	Log	0.339	-3.65	0.11
Nitrate	$5.5 \times 10^{-4}$	Semilog	$1.79 \times 10^{-3}$	$-3.22 \times 10^{-3}$	$7.3 \times 10^{-4}$
Boron	$2.3 \times 10^{-4}$	Log	0.276	-4.29	0.13
Silica	0.0046	Log	0.555	-3.54	0.05

<u>Saline River</u>					
<u>Ion</u>	<u>Mean</u>	<u>Relationship</u>	<u>a</u>	<u>b</u>	<u><math>\sigma^*</math></u>
Calcium	0.32	Semilog	0.207	-0.03	0.05
Magnesium	0.12	Constant	0.123		0.02
Sodium	0.54	Semilog	-0.231	0.930	0.06
Potassium	0.016	Log	0.326	-2.45	0.21
Iron	$1.5 \times 10^{-4}$	Log	0.472	-5.02	0.43
Hydrogen	$1.2 \times 10^{-6}$	Log	0.507	-7.03	0.28
Bicarbonate	0.19	Log	0.377	-1.44	0.10
Sulfate	0.28	Constant	0.280		0.05
Chloride	0.52	Semilog	-0.210	0.88	0.06
Fluoride	0.0014	Log	0.339	-3.52	0.15
Nitrate	0.0017	Semilog	$2.44 \times 10^{-3}$	$-2.46 \times 10^{-3}$	$1.9 \times 10^{-3}$
Boron	$4.3 \times 10^{-4}$	Log	0.108	-3.60	0.32
Silica	0.0090	Log	0.545	-3.22	0.03

Table 6-2 (Contd.). Selected ion proportion relationships to discharge.

<u>Wind River</u>					
<u>Ion</u>	<u>Mean</u>	<u>Relationship</u>	<u>a</u>	<u>b</u>	<u><math>\sigma^*</math></u>
Calcium	0.51	Log	0.085	-0.53	0.04
Magnesium	0.21	Constant	0.211		0.05
Sodium	0.26	Log	-0.180	-0.11	0.07
Potassium	0.016	Log	0.229	-2.45	0.14
Iron	$4.2 \times 10^{-4}$	Log	0.423	-4.67	0.37
Hydrogen	$4.6 \times 10^{-6}$	Log	0.595	-7.13	0.32
Bicarbonate	0.62	Log	0.079	-0.42	0.03
Sulfate	0.34	Log	-0.157	-0.06	0.06
Chloride	0.037	Log	-0.139	-1.09	0.16
Fluoride	0.0044	Constant	$4.42 \times 10^{-3}$		0.002
Nitrate	0.0020	Log	0.414	-3.95	0.37
Boron	$8.3 \times 10^{-4}$	Log	0.144	-3.63	0.34
Silica	0.034	Log	0.394	-2.59	0.25

Ion proportions are well estimated by the above simple relations to the discharge. For the major ions, the standard deviations of the residuals were small and generally correspond to errors of less than 0.05 in the major ion proportions. For the minor constituents the variations about the predicted proportions were more significant, with the standard deviations of the residuals corresponding to errors of about the same magnitude as the average proportions. The accuracy of the chemical determinations for the minor constituents is, however, also less than for the major constituents.

In the application of the logarithmic relation, Equation 6-4, it is necessary to apply corrections for the bias introduced. Generally these corrections are needed only for the minor constituents although corrections are applied for all constituents using the logarithmic relation. The correction amounts to increasing the value of the intercept  $b$  by  $1.15(\sigma^*)^2$ .

#### 6.5 Stochastic Components

Stochastic components for the ion proportions cannot be determined because of the composite nature of the data. Since the samples for which chemical analyses were made are composite samples made up of varying numbers of individual samples, the effect of the individual stochastic components are no longer apparent. Therefore, no conclusive study may be made of the stochasticity of the ion proportion without additional data or at least some prior knowledge of the behavior of the stochastic components.

The stochastic components of the ion proportions for a given composite sample must be interdependent due to the constraint that both the sum of the anion proportions and the sum of the cation proportions must equal unity. Again this interdependence cannot be determined due to the composite nature of the available data.

Since there is no acceptable method for analyzing or determining the stochastic components for the ion proportions, this will be left for future study when the necessary data becomes available. Stochastic simulation of the individual inorganic constituents will not be done in this study.

#### 6.6 Closing Remarks

It was found that proportions of various constituents are well estimated by either a logarithmic or a semilogarithmic relation with flow or the proportions are constant. The apparent inconsistency of using both logarithmic and semilogarithmic relations for ions on the same stream, which resulted from observed data, did not have any adverse effects. That is, the sum of anion (or cation) proportions as given by the relations are very nearly unity regardless of the value of discharge. Most ions followed the logarithmic relation as was expected. No relation was found between ion proportions and time of year.

The accuracy of results is good, as indicated by the standard deviations of the residuals. Major ion proportions were found to be estimated with a standard error of about 0.05 or less. The minor constituents' proportions were not as well estimated. The errors in predicting the proportions of minor constituents were relatively large and often of the same magnitude as the average proportion of the constituent. The residual errors observed are comparable to the random errors expected with sampling.

The application of the methods used here are fairly simple. First the constituent proportions are calculated and two regressions performed with  $\log Q$ , one using the logarithms of the proportions. That regression showing the highest explained variance is then chosen. In cases of very low explained variance or where the regressions are statistically insignificant, a constant relation should be considered.

## Chapter 7 CONDUCTIVITY AS RELATED TO SPECIFIC ION CONCENTRATIONS

The conductivity of a water sample is a direct result of the inorganic ions in solution. The basic theory has been available for making the relation between the ions in solution and the conductivity of the solution. However, it has not previously been applied to natural water due to its complexity. Both a theoretical equation and a simplified equation are developed and applied in this chapter. This relationship along with the previously developed relationships relating conductivity and constituent proportions to discharge allows the extraction of water quality information from discharge measurements alone.

### 7.1 Modes of Expression

Conductivity, which is simply a measure of the ability of a solution to carry an electrical current, may be expressed as the reciprocal of the resistivity of the solution. Thus the conductivity  $\kappa$  may be expressed as

$$\kappa = \frac{1}{\rho} \quad , \quad (7-1)$$

where  $\rho$  is the resistivity of the solution. Commonly, micromhos per centimeter are used for the units for the conductivity of natural waters. The terms conductance and conductivity are generally used to denote the same quantity with the same units of expression.

Chemical salts when dissolved in water readily dissociate into ions which support the flow of electrical current. Without the presence of these ions water will not conduct to any appreciable extent (Hem, 1970). Since the conductance of an electrolytic solution results directly from the dissolution of salts, the solution is often described in terms of its conductance.

The ratio of the conductivity of a solution to the concentration of the solution is called the equivalent conductance. The equivalent conductance  $\Lambda$  of a solution containing a single salt is the conductance divided by the number of gram equivalents per liter of the salt present in solution. Thus for a solution containing a single salt, the equivalent conductance is given by

$$\Lambda = \frac{2\kappa}{\sum_i m_i z_i} \quad , \quad (7-2)$$

where  $m$  and  $z$  refer to the concentration in moles per liter and charge (absolute value) of the  $i$ -th ion resulting from the dissociation of the salt. The units for equivalent conductance are commonly micromhos/cm per milliequivalent/liter (or  $\mu\text{U} - \text{cm}^2/\text{equiv.}$ ). The equivalent conductance may further be divided into the equivalent conductances due to each of the individual ions present. Thus for an electrolyte which results in two ions

$$\Lambda = \lambda_1 + \lambda_2 \quad , \quad (7-3)$$

where  $\lambda_1$  and  $\lambda_2$  are the equivalent conductances of the two ions. For a more complicated solution involving many ions, the relationship is very similar:

$$\kappa = \sum_i m_i z_i \lambda_i \quad . \quad (7-4)$$

It should be noted at this point that the above equation provides a linear relation between the concentrations of the various ions in solution and the total conductance, provided that the equivalent conductances  $\lambda$  remain as constants. As will be shown later, the equivalent conductances do change with temperature, ionic concentration and the nature of the solution. Fortunately the effects of these are both predictable and gradual so that these effects may be taken into account, leaving a relationship which is virtually linear within a limited range of concentrations for a given temperature and type of solution.

Since the equivalent conductances do change with the type and concentration of solution, another quantity is used as a basic reference point. This is the equivalent conductance at infinite dilution, that is, the limiting equivalent conductance as the solution concentration approaches zero and is denoted by a superscript zero. Values of  $\Lambda^\circ$  and  $\lambda^\circ$  are listed in Tables A7-1 and A7-2 of the Appendix. Illustrating the effect of concentration upon equivalent conductance, Figure 7-1 shows the relationship for a simple single salt solution of  $\text{CaCl}_2$ .

Electrical conductance, or conductivity, is often also referred to in terms of specific conductance, that is, the conductance in mhos of a cubical element of solution one centimeter on a side with electrodes one centimeter square and one centimeter apart. The values of conductance and specific conductance are the same, provided units of mhos per centimeter and mhos are used respectively.

Since conductance is also temperature dependent, all values must be referenced to a temperature. Thus the proper units of conductance are "mhos per centimeter at  $t^\circ\text{C}$ ." For most ions, the conductivity increases about two percent with each degree increase in temperature. Values for measured conductance of natural waters and also for the reference values of  $\Lambda^\circ$  and  $\lambda^\circ$  are usually referenced to  $25^\circ\text{C}$ . Therefore for a solution at temperature  $T^\circ\text{C}$  with a measured conductivity of  $\kappa_T$ , the conductivity at  $25^\circ\text{C}$  may be obtained by the formula

$$\kappa_{25} = \kappa_T [1 - 0.02(T-25)] \quad , \quad (7-5)$$

presented by Tanji and Biggar (1972). An easier method for temperature correction, which is commonly used, is described in the next section.

### 7.2 Conductivity in Water Quality

Conductivity has long been recognized as an indicator of the total concentration of salts. As such, it has been included in the chemical analyses done by the United States Geological Survey. Also due to the ease of conductance measurements, conductance is often measured on a daily basis along with the flow, although the chemical analyses on the same stream are made much less frequently (Brown, et al., 1970; Hem, 1970).

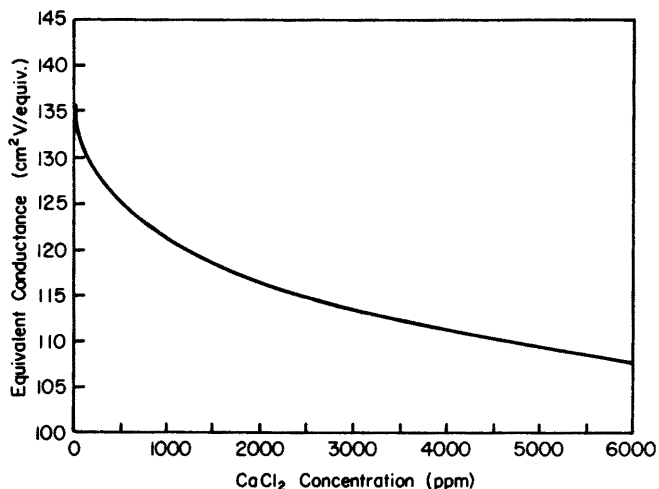


Figure 7-1. Equivalent conductance versus concentration of calcium chloride (Chemical Rubber Company, 1964).

The range of conductivity values is quite large, from as low as 50 micromhos/cm to as high as 50,000 or more (Hem, 1970). The accuracy of measurements of conductivity is estimated by Hem (1970) to be from  $\pm 2$  to  $\pm 5$  percent with careful operation of the measurement equipment. Other sources (Rainwater and Thatcher, 1960; Brown, et al., 1970) give the accuracy as  $\pm 2$  to  $\pm 3$  percent. Field measurements if carefully made are of comparable accuracy with laboratory tests. Values of conductivity commonly are determined by using a wheatstone bridge in which the conductance cell is the unknown resistance. Since the cell is not likely to be of exactly the right dimensions, a cell constant  $A_c$  is used. The relation between the conductance  $\kappa$  and the resistance  $R$  of the solution being measured is given by

$$R\kappa = A_c \quad (7-6)$$

Since adjusting the temperature of the sample to exactly 25°C would be difficult and since the use of Equation 7-5 is only approximate, another method for adjusting the conductivity measurements to 25°C is used which is even easier. By measuring the resistance of a 0.00702 Normal potassium chloride solution at the water sample temperature and knowing that the conductivity at 25°C for this solution is exactly 1000 micromhos/cm, a new cell constant may be found which takes into account the temperature of the solution and gives the sample's conductance at 25°C. Thus by measuring both the resistance of this "standard cell" and the resistance of the unknown sample, the conductivity of the sample at 25°C may easily be calculated by

$$\kappa = \frac{1000 R_{KCl}}{R} \quad (7-7)$$

Where  $R$  is the resistance of the sample and  $R_{KCl}$  is the resistance of the standard cell of 0.00702 N potassium chloride (Brown, et al., 1970).

A rough check for the total dissolved solids is often made using the following relation

$$\kappa(0.65 \pm 0.10) = \text{TDS} \quad (7-8)$$

where TDS is the total dissolved solids in parts per million (Brown, et al., 1970). The constant factor in Equation 7-8 may be less than 0.55 for very alkaline or acid waters and more than 0.75 for saline waters (American Public Health Assoc., 1965). Hem (1970) reports values which range from 0.54 to 0.96 with the highest values for waters high in sulfate. He indicates that a regression to determine the constant for a particular stream may result in accurate relationships not only for TDS but also for individual ions. While this equation is very useful on many streams, it has a number of drawbacks. First it is empirical and may not be applied to any new stream without applying another regression. Errors in the regression may prove to be serious particularly for extrapolation outside the range of the regression data. The approach also implicitly assumes that the extent of dissociation is a constant, that the relative proportions of ions remain constant, and that the values of  $\lambda$  remain fixed. These assumptions are not generally valid. While the relative proportions of ions may tend to remain constant, there is evidence that this is not generally the case. The extent of dissociation is very concentration dependent and only for very dilute solutions or solutions of a very limited concentration range could the dissociation be assumed constant. Likewise, the values of  $\lambda$  are concentration dependent and may only be assumed fixed within limited ranges of concentration. For these reasons this type of relationship is rejected in favor of a more reliable and correct relationship between conductivity and ion concentration which takes into account the concentration dependence.

Fair et al. (1968) extended the relationship of Equation 7-8 by applying temperature correction of two percent per degree centigrade and expressed the results both in terms of milliequivalents per liter and milligrams per liter. The equations are claimed to be accurate within 20 percent for waters with pH in the range of 5 to 9 and temperatures between 10 and 40°C and of less than 1000 mg/l concentration. The equations may be written as

$$\text{Dissolved Salts (meq/l)} = 0.008 \kappa_T / (1.02)^{T-25} \quad (7-9)$$

and

$$\text{Dissolved Salts (mg/l)} = 0.45 \kappa_T / (1.02)^{T-25} \quad (7-10)$$

where conductivity is in micromhos per centimeter. It should be noted that in the original form, apparently due to a type setting error, Fair et al. (1968) give the equations with the temperature correction inverted.

Rossum (1949) determined a somewhat more precise conductance method for checking chemical analyses which has been adopted in standard methods (American Public Health Assoc., 1965) and by the United States Geological Survey (Brown, et al., 1970). Essentially the method is to dilute the sample so that the conductance is between 90 and 120 micromhos/cm. This corresponds to approximately a solution with a strength of 0.001 Normal for which the values of  $\lambda$  are estimated by Rossum. Knowing the dilution ratio

$$D = \frac{V_s + V_w}{V_s}, \quad (7-11)$$

where  $V_s$  is the volume of the original sample and  $V_w$  is the volume of distilled dilution water added, a "diluted conductance"  $\kappa_d$  may be determined by

$$\kappa_d = \kappa D - (D-1)\kappa_w, \quad (7-12)$$

where  $\kappa$  is the conductance of the diluted sample (i.e., 90 - 120 micromhos/cm) and  $\kappa_w$  is the conductance of the distilled water. The value of  $\kappa_d$  should be equal to the value of conductance calculated using the conductance factors furnished by Rossum (1949) and added to by the American Public Health Association (1960). The sum of the ion concentration-conductance factor products is checked against  $\kappa_d$  to insure that the chemical analysis did not overlook any major ions and was generally accurate. The conductance factors are shown in Table 7-1 along with the values of  $\lambda^\circ$  for the same ions. In comparing the values given in Table 7-1, it appears that the conductance factor for carbonate may be in error since the conductance factor (i.e., equivalent conductance at approximately 0.001N) is greater than the value of  $\lambda^\circ$ . Since no factors are given for hydrogen or hydroxyl ions and since the conductances of these ions are quite high, the method is not applicable to samples outside a pH range of six to nine. Also it is not applicable to samples having an initial conductance of less than 90 micromhos/cm. Rossum's method is generally used by chemists as a check that no important ions have been left out of an analysis and that the analysis contains no gross errors. Rossum recommends that a recheck of the analysis is needed if the computed diluted conductance is more than 1.5 percent higher or 2.0 percent lower than the measured diluted conductance. Brown et al. (1970) feel that this degree of accuracy is not attained in routine water analyses.

Table 7-1. Conductance factors used in Rossum's method\* for checking chemical analyses.

Ion	$\lambda^\circ$ micromhos/meq/l at 25°C	Conductance factor micromhos/meq/l at 25°C
Bicarbonate	44.5	43.6
Calcium	59.6	52.0
Carbonate	69.3	84.6
Chloride	76.4	75.9
Magnesium	53.0	46.6
Nitrate	71.5	71.0
Potassium	73.5	72.0 †
Sodium	50.1	48.9
Sulfate	80.0	73.9

\*(Rossum, 1949)

†(APHA, 1960)

The methods presented later in this chapter are basically an extension of the work of Rossum. Rather

than require a dilution of the sample water, however, the equivalent conductances will be calculated for each of the ions in solution at the sample's ionic strength. In this way the available undiluted conductance data will be of use in checking chemical analyses or for use in the extraction of water quality information.

The idea of computing the conductivity effect of each ion separately is not new. A number of investigators, primarily in the area of soil chemistry, have used empirical or semiempirical methods with varying degrees of success (Campbell, 1948; Tanji, 1969a; McNeal et al., 1970; Tanji and Biggar, 1972). Kohlrausch's law states that, for very dilute solutions made up of a strong electrolyte, that is, made up of a salt which completely dissociates, the equivalent conductance is given by

$$\Lambda = \Lambda^\circ - B\sqrt{C}, \quad (7-13)$$

where B is a constant for the salt and C is the concentration of the salt solution (Butler, 1964). This may be expanded to the individual ions resulting from the salt,

$$\lambda_i = \lambda_i^\circ - b_i\sqrt{C}, \quad (7-14)$$

where b is a constant for the i-th ion good only for this one particular salt solution with C the concentration of the salt solution. For a multisalt solution, the appropriate form is

$$\lambda_i = \lambda_i^\circ - b_i\sqrt{I}, \quad (7-15)$$

again where b is a constant but now is independent of the type of solution and good for any salt solution. The salt concentration C is in this case replaced by I, the ionic strength of the solution, given by

$$I = \sum_i \frac{m_i z_i^2}{2}, \quad (7-16)$$

where m refers to the concentration in moles per liter of the i-th ion and z is that ion's charge. Although this approach is not valid for concentrated solutions it may be used with good results for natural waters of moderate concentration, up to a concentration of approximately 1000 parts per million dissolved solids.

Tanji and Biggar (1972) used an approach very similar to this except that they used

$$\lambda_i = \lambda_i^\circ - b'\sqrt{c_i}, \quad (7-17)$$

where c is the concentration of the i-th ion. The problem with this approach is that the effect of all other ions has been lumped into the constant b' which must be derived empirically for each stream and is not transferable. Unless the ionic strength I and the concentrations c are of a constant proportionality, the values will be either overpredicted or underpredicted depending on the ratio of I to c. Since the proportions of the ions do not vary greatly on a given stream and there were compensating errors, they found this approach gave fairly reliable results for their data.

### 7.3 Equivalent Conductivity Formulas

The equivalent conductance of an ion is commonly known to decrease as the salt concentration of the



solution increases. This relationship between ionic concentration and equivalent conductance has been studied for some time by physical chemists. The choice of a formula to apply depends in part upon the concentration of the solution: the higher the concentration, the more complex the required formula.

A basic formula (Robinson and Stokes, 1970) used for the equivalent conductance of a salt is

$$\Lambda = \left( \Lambda^\circ - \frac{\phi_1' \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right) \left( 1 - \frac{\phi_3 \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right). \quad (7-18)$$

There are two correction terms contained in this equation which account for the deviations in the equivalent conductance from that at infinite dilution. The first is a correction for what is known as the electrophoretic effect. This effect arises from the interaction of the motion of the ions on one another. As an ion moves through the solution, it tends to carry along with it part of the surrounding water media due to the viscosity of the water. Other ions must then either move with or against this "flow" with the net result being a reduction in average velocity.

The second correction term, the right hand portion of Equation 7-18, is for what is called the relaxation effect. It is used to account for the forces produced as a result of disturbances in the spherical symmetry of the ionic atmosphere caused by the motion of the ions (Robinson and Stokes, 1970; Fuoss and Accascina, 1959).

The electrophoretic effect tends to be approximately twice the relaxation effect for simple 1:1 electrolytes and approximately equal for 2:2 electrolytes.  $\phi_1'$ ,  $\phi_2$  and  $\phi_3$  are functions of the solution and  $I$  is the ionic strength of the solution given by Equation 7-16.

For a salt separating into only two ions,  $\phi_1'$ ,  $\phi_2$  and  $\phi_3$  are given by

$$\phi_1' = 30.325(z_1 + z_2), \quad (7-19)$$

$$\phi_2 = 0.3291 \sqrt{a_1 a_2}, \quad (7-20)$$

and

$$\phi_3 = 0.7853 z_1 z_2 \frac{q}{1 + \sqrt{q}}, \quad (7-21)$$

where  $a_1$  and  $a_2$  are ion size parameters and  $q$  is a mobility function given by

$$q = \frac{z_1 z_2}{z_1 + z_2} \cdot \frac{\lambda_1^\circ + \lambda_2^\circ}{z_2 \lambda_1^\circ + z_1 \lambda_2^\circ},$$

or

$$q = \frac{(\lambda_1^\circ + \lambda_2^\circ)/(z_1 + z_2)}{\lambda_1^\circ/z_1 + \lambda_2^\circ/z_2}. \quad (7-22)$$

For symmetrical electrolytes,  $q = 1/2$ , and  $\phi_3$  reduces to  $0.230 z_1 z_2$ . The constants 30.325, 0.3291 and 0.7853 result from the theoretical derivation of

these equations and are dependent on the dielectric constant, viscosity and temperature. The values used here are from Robinson and Stokes (1970). Computer programs are readily available for calculating the theoretical conductance of single salt solutions (for example, see de Maine, 1965).

The equivalent conductivity formula for individual ions is very similar to that for a salt:

$$\lambda_i = \left( \lambda_i^\circ - \frac{\phi_1 \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right) \left( 1 - \frac{\phi_3 \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right), \quad (7-23)$$

$$\text{where } \phi_1 = 30.325 z_i, \quad (7-24)$$

and  $\phi_2$  and  $\phi_3$  are as previously defined provided that the ions result from a simple salt which produces only two ions. It should be noticed that the expression  $1 + \phi_2 \sqrt{I}$  which appears in both terms is of minor importance, affecting the results only for concentrated solutions. For very dilute solutions this expression may be accurately taken to be one. The value of  $\phi_2$  is very nearly one for most ions.

#### 7.4 Relaxation Term for Multi-ion Solutions

The relaxation term requires a more involved treatment in the case of more than two ions in solution. The evaluation of this term given here will follow the form presented in a classic paper on conductivity by Onsager and Fuoss (1932). The relaxation term,

$$\frac{\phi_3 \sqrt{I}}{1 + \phi_2 \sqrt{I}}, \quad (7-25)$$

for a multi-ion solution requires a new interpretation be given to  $\phi_2$  and  $\phi_3$ . The ionic strength  $I$  is still defined as before.  $\phi_2$  is defined as follows

$$\phi_2 = 0.3291 \bar{a}_i, \quad (7-26)$$

where  $\bar{a}_i$  is an average between the size parameter of the ion under consideration and all opposing ions. The subscript  $i$  refers to the ion under consideration. One possible evaluation for  $\bar{a}_i$  which is used here is a weighted geometric mean ion size given by

$$\bar{a}_i = \frac{\sum_j (c_j \sqrt{a_i a_j})}{\sum_j c_j}, \quad (7-27)$$

where  $j$  refers to only those ions of opposite charge from the  $i$ -th ion and  $c$  refers to the concentration in milliequivalents per liter.

The denominator  $1 + \phi_2 \sqrt{I}$  of Equation 7-25 was not included in the original Onsager and Fuoss presentation but was later included and is presently used in all equations (Harned and Owen, 1958; Robinson and Stokes, 1970).

Evaluation of the  $\phi_3$  term is much more complicated for a multi-ion solution due to the complexity of interactions between the ions. Onsager and Fuoss (1932) gave the evaluation of  $\phi_3$  as

$$\phi_3 = A z_i s_i \sum_{n=0}^{\infty} C_n r_i^{(n)}, \quad (7-28)$$

where A is a physical constant. Evaluating the constant for an aqueous solution at 25°C using the value given in Robinson and Stokes (1970),  $\phi_3$  becomes

$$\phi_3 = 0.7853 z_i s_i \sum_{n=0}^{\infty} C_n r_i^{(n)}. \quad (7-29)$$

In this expression z is the charge, s is the sign of the charge,  $C_n$  are constant coefficients from a power series expansion and  $r_i^{(n)}$  are terms dependent on the nature of the solution. The first six terms of the  $C_n$  terms are contained in Table A7-3, appendix.

Six terms are used in this work although examination would probably show that four or fewer terms would be sufficiently accurate. The terms  $r_i^{(n)}$  are calculated from a recursive relation

$$r_i^{(n)} = \sum_k (2h_{ik} - \delta_{ik}) r_k^{(n-1)} \quad \text{for } n \geq 1, \quad (7-30)$$

where  $\delta_{ik}$  is the Kronecker delta symbol ( $\delta_{ik} = 0$  for  $i \neq k$ ;  $\delta_{ik} = 1$  for  $i = k$ ). The term  $2h_{ik} - \delta_{ik}$  is often written as  $t_{ik}$  so that

$$r_i^{(n)} = \sum_k t_{ik} r_k^{(n-1)} \quad \text{for } n \geq 1. \quad (7-31)$$

Now

$$h_{ik} = \delta_{ik} \sum_p \frac{\mu_p \omega_p}{\omega_p + \omega_k} + \frac{\mu_k \omega_k}{\omega_i + \omega_k}, \quad (7-32)$$

where  $\mu$  is the relative mobility of the ion and  $\omega$  is its mobility. These quantities are easily calculated for all ions as

$$\mu_i = \frac{I_i}{I} = \frac{c_i z_i}{\sum_k c_k z_k}, \quad (7-33)$$

and

$$\omega_i = \frac{300}{96,500} \frac{\lambda_i^\circ}{z_i}, \quad (7-34)$$

or

$$\omega_i = A \frac{\lambda_i^\circ}{z_i},$$

where A is an invariant constant which cancels out during the calculation of h. Thus  $\omega'$  may be used in place of  $\omega$  where

$$\omega'_i = \frac{\lambda_i^\circ}{z_i}, \quad (7-35)$$

The evaluation of the  $r^{(0)}$  terms, needed in Equation 7-30 to calculate the other  $r^{(n)}$  terms, is given by

$$r_i^{(0)} = z_i s_i - \frac{z_i}{\lambda_i^\circ} \frac{\sum_k (z_k \mu_k s_k)}{\sum_k (z_k \mu_k / \lambda_k^\circ)}. \quad (7-36)$$

## 7.5 Modifications to Equivalent Conductivity Calculations

Since the method of calculating the relaxation term given in the last section is very complex, some simplifying modification may be desirable despite the possibility of introducing greater inaccuracies.

For a two ion salt  $\phi_3$  is evaluated as Equation 7-21

$$\phi_3 = 0.7853 z_1 z_2 \frac{q}{1 + \sqrt{q}},$$

where Equation 7-22

$$q = \frac{(\lambda_1^\circ + \lambda_2^\circ) / (z_1 + z_2)}{\lambda_1^\circ / z_1 + \lambda_2^\circ / z_2}.$$

An appealing modification for a multi-ion solution is to calculate  $\phi_3$  for the i-th ion as

$$\phi_3 = 0.7853 z_i z_0 \frac{q}{1 + \sqrt{q}}, \quad (7-37)$$

where  $z_0$  is the average opposing charge and q is now calculated as

$$q = \frac{\sum c_i \lambda_i^\circ / \sum c_i z_i}{\sum c_i (\lambda_i^\circ / z_i) / \sum c_i}. \quad (7-38)$$

This simplification could be carried a step further by assuming q as a constant equal to 0.5 and setting  $z_0$  equal to  $z_i$  making

$$\phi_3 = 0.230 z_i^2. \quad (7-39)$$

A similar simplification to the  $\phi_2$  term may also be made by calculating the term as

$$\phi_2 = 0.3291 a_i. \quad (7-40)$$

The conductivity formula, Equation 7-23, under the approximations of Equations 7-39 and 7-40 now becomes

$$\lambda_i = \left( \lambda_i^\circ - \frac{30.325 z_i \sqrt{I}}{1 + 0.3291 a_i \sqrt{I}} \right) \left( 1 - \frac{0.230 z_i^2 \sqrt{I}}{1 + 0.3291 a_i \sqrt{I}} \right) \quad (7-41)$$

Referring back to Equation 7-15,  $\lambda_i = \lambda_i^\circ - b_i \sqrt{I}$  and comparing with Equation 7-23 neglecting the cross product term,

$$b_i = \frac{\phi_1 + \phi_3 \lambda_i^\circ}{1 + \phi_2 \sqrt{I}} \quad (7-42)$$

Evaluating  $\phi_2$  and  $\phi_3$  according to the approximations given by Equations 7-40 and 7-39, and evaluating  $\phi_1$ ,

$$b_i = \frac{30.325 z_i + 0.230 z_i^2 \lambda_i^\circ}{1 + 0.3291 a_i \sqrt{I}} \quad (7-43)$$

Calculations of this form, Equation 7-41 or 7-15, are much easier to apply than the complete formula. Using Equation 7-41, this form of calculation was applied and compares well with both the measured conductivity values and the values computed by the more complicated formula. The success of this method is partly due to compensating errors with the effects of some ions overestimated, and others underestimated. The differences in the two approaches are not of great concern except for concentrated solutions where the result may be as much as six percent difference ( $\text{Na}_2\text{SO}_4$  solution, ionic strength of 0.14). As a rough guide this approach appears applicable to solutions with an ionic strength of 0.02 or less.

#### 7.6 Effect of Undissociated Ions

Ions which have not dissociated but have formed complexes or ion pairs must be taken into account in conductivity calculations. The conductivity of a natural water solution is often very much below that calculated assuming complete dissociation of the ions. This is because the complexing of ions results in a net reduction in the ionic strength and mole equivalents in solution. Since the total concentrations of various ions and ion radicals in all forms, both combined and uncombined, are typically determined in chemical analysis, it is the total concentrations that are of prime interest. An exception is the hydrogen ion or pH. For conductivity calculations, however, a procedure for calculating the actual ion concentrations in solution, must be used.

Procedures for calculating the various forms actually found in solution may be found in any number of chemistry texts (Garrels and Christ, 1965; Stumm and Morgan, 1970; and Butler, 1964) and have been used by soil chemists (Tanji et al., 1967; Tanji, 1969b). For cases of interest here, calculation of the various forms essentially requires the solution of a set of quadratic equations which are easily written using dissociation constants. The set of equations in this case may be easily solved by an iterative calculation. The association-dissociation reaction may be written



where M is a metal ion and L is a ligand. The formation constant K is given by

$$K = \frac{\{ML\}}{\{M\}\{L\}} \quad (7-45)$$

where the quantities within braces represent activities. The reciprocal of the formation constant is often also used in the literature and is referred to here as  $K'$ . The values of the formation constants are temperature dependent but not to the extent affecting the results enough to require correction. The values used in this study are those for approximately 25°C. The use of a constant K also assumes that the solution is at an equilibrium condition. This assumption is valid provided the reaction rates are sufficiently large with respect to some characteristic time. These assumptions are all made here.

In solving the dissociation equations, the equations are changed from being in terms of activities to being in terms of concentrations:

$$K' = \frac{\{M\}\{L\}}{\{ML\}} = \frac{\gamma_M \gamma_L [M][L]}{\gamma_{ML} [ML]} \quad (7-46)$$

where the quantities within brackets are concentrations in moles per liter and the  $\gamma$  terms refer to the activity coefficients which in this study are taken to be that given by the Guntelberg approximation (Stumm and Morgan, 1970) as

$$\log \gamma_i = \frac{-0.51 z_i^2 \sqrt{I}}{1 + \sqrt{I}} \quad (7-47)$$

Other approaches for calculating the activity coefficient (Stumm and Morgan, 1970; Klotz, 1950; Kielland, 1937) may also be used with only minor differences in results. Hem (1961) has developed graphs suitable for determining activity coefficients for all ions found in natural waters.

The most important associations between anions and cations are those of the sulfate complexes. For waters high in sulfate, a great deal of complexing can be expected, primarily  $\text{CaSO}_4^\circ$  and  $\text{NaSO}_4^-$ , with some  $\text{KSO}_4^-$ .

For waters high in bicarbonate similar complexes involving calcium, magnesium and sodium can be expected. However, since the concentrations of bicarbonate rarely exceed 400 ppm this effect may often be neglected completely.

Carbonate complexes with calcium and magnesium and to some extent with sodium but since the total carbonate concentration is very small except in very high pH waters these complexes may normally be ignored.

There will be some  $\text{HSO}_4^-$  complexing observed at very low pH values. The  $\text{pK}'$  value equals approximately 2.0 for  $\text{HSO}_4^-$ . It should be noted that the prefix p as in pH or pK denotes a minus the logarithm of the quantity. That is a value of  $\text{pK}'$  of 2 means the value of  $K'$  equals  $10^{-2}$ .

Complexing involving the hydroxyl radical will be primarily with magnesium, but also some complexing with calcium will occur to a lesser extent. This complexing will not be of importance except at very high pH values ( $\text{pH} > 10$ ).

Table 7-2 gives values for log K for these ion complexes (Garrels and Christ, 1965). Additional values from various reference sources are given in Table A7-4 of the Appendix with some guidelines to the importance of the various complexes. Nitrate complexes are included in the Appendix although they are rarely of importance. Manganese complexes with bicarbonate and sulfate have not been included although they are important for waters with appreciable manganese (the reader is referred to Hem, 1963).

Table 7-2. Formation constants for several dissolved species in aqueous solutions at 25°C.

Cations	OH <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Anions CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>
		log K			
H <sup>+</sup>	14.0	6.4	10.33	2	--*
K <sup>+</sup>	--	--	--	0.96	--
Na <sup>+</sup>	- 0.7	-0.25	1.27	0.72	--
Ca <sup>++</sup>	1.30	1.26	3.2	2.31	--
Mg <sup>++</sup>	2.58	1.16	3.4	2.36	--

\*Denotes no measurable association (Garrels and Christ, 1965)

In this study provisions were made for sulfate, bicarbonate, carbonate and hydroxyl complexes although the last two can be neglected in all but the highest pH waters.

In calculating the amount of carbonate complexing, the carbonate activity is calculated by using the formation constant for bicarbonate, pH of the solution and bicarbonate concentration.

Figures 7-2, 7-3, 7-4 and 7-5 depict the relation between the ion activity ratios of complexed to uncomplexed cations and the activity of ligands of interest in natural waters. From these diagrams it is fairly easy to determine for a given ligand activity the degree of complexing. If the cation activity is also known, the seriousness of neglecting this complexing may be determined.

Although the activities are rarely known, by using approximate concentrations and approximate activity coefficients the activities may be determined with sufficient accuracy to at least decide if the dissociation may be neglected. For example if the

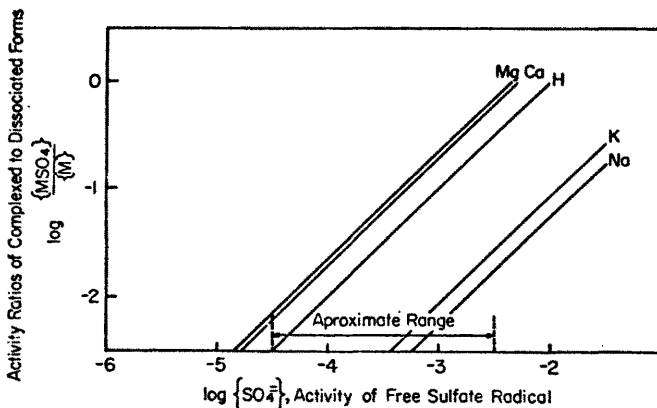


Figure 7-2. Sulfate complexing.

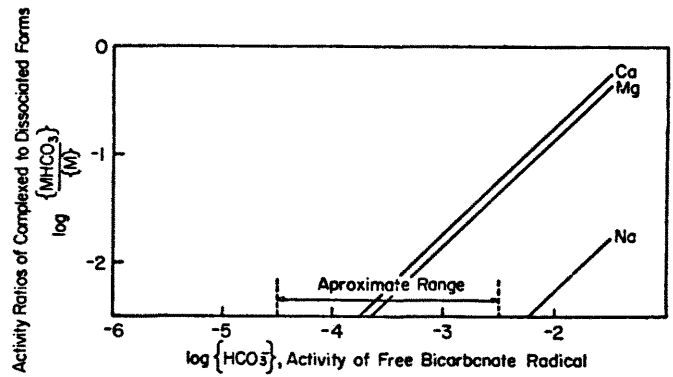


Figure 7-3. Bicarbonate complexing.

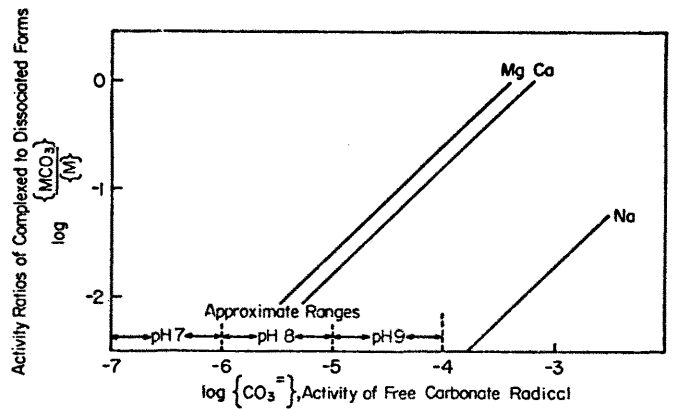


Figure 7-4. Carbonate complexing.

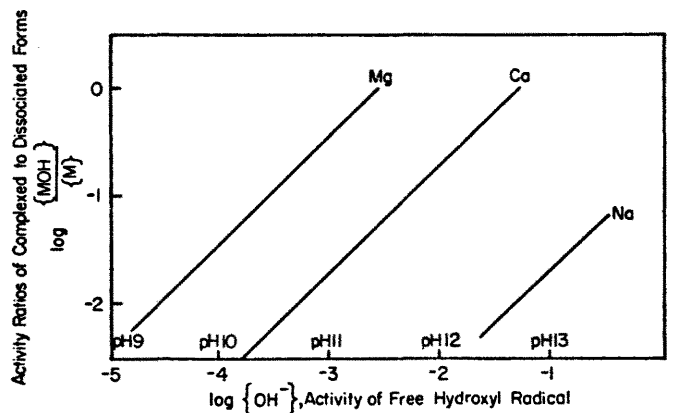


Figure 7-5. Hydroxyl complexing.

sulfate concentration determined by chemical analysis is one millimolar, the free sulfate ion activity could be roughly approximated as 10<sup>-3</sup> moles per liter. From Figure 7-2, it is seen that the sulfate complexing is insignificant for potassium and sodium (less than one percent) and could be ignored. For magnesium, calcium and hydrogen, the sulfate complexing appears to be very high, 30 percent or more, and should be considered if the concentrations of these cations are significant. However, if the sulfate concentration, again as a rough estimate for the free sulfate ion activity, is less than 0.1 millimolar, all complexed forms could be neglected. The magnesium-sulfate complex in this case would have a concentration of less than five percent of the free magnesium ion in solution. For the

other ions, the percent of the cation being complexed is even less.

### 7.7 Application of Conductance Equations

In applying the two equivalent conductivity equations, Equations 7-23 and 7-41, corrections must first be made for the undissociated ions found in solution. This is done with the aid of appropriate dissociation constants which are given in Table 7-2 of the text and Table A7-4 of the Appendix.

After determining the various ionic constituents of the solution, the conductivity equations may be applied. Basic reference data required to apply the equations includes the ion size, parameter ionic charge and its sign, and the equivalent conductance value at infinite dilution for each of the ionic species. These values are included in Table A7-2 of the Appendix for all ions considered in this study.

Both of full equation (7-23) and the approximate equation (7-41) have been applied to a number of samples from not only the five streams studied throughout this work but also tabulated data from careful chemical studies of single salt solutions and data taken from the Kiskiminetas River at Leechburg, Pennsylvania, which has very acidic water. A representative sample of typical results is shown in Table A7-5 of the Appendix.

The approximate equation gave results virtually identical to those given by the full equations. For concentrations of less than approximately 1000 ppm, the approximate equation appears to be accurate to at least  $\pm 1$  percent.

The full equation gave results with percent differences having a mean of 0.68 percent and a standard deviation of 3.74 percent for 784 samples from the streams of this study and appears to be accurate to at least  $\pm 1$  percent for concentrations of 10,000 ppm and possibly higher. Both equations tended to give high results for the conductivity. In calculating errors, only those samples were used for which the anion-cation balance was within the limits recommended by the American Public Health Association (1965).

A sample conductivity calculation is shown in Table A7-6 of the Appendix. These methods of calculation appear to be applicable to natural waters over a very large pH range, at least three to ten, and a broad range of concentrations. The most important consideration, which is also the most probable source of error, is accounting for all appreciable undissociated dissolved species. The results could possibly be improved if an optimization were made in the choice of the formation constants (they are often determined by conductivity measurements and therefore this would be justified somewhat) or in the choice of ion size parameters which are also empirical in nature. Monk (1961) shows that the value obtained for the formation constant using a conductance method of determination depends upon the ion size parameter used, in addition to the form of the conductance equation (Harned and Owen, 1958). For dilute solutions of single salts where the degree of complexing is very small, Harned and Owen (1958) have shown that  $K$  may be determined from

$$K = \frac{\kappa_1}{\kappa_2 C}, \quad (7-48)$$

where  $C$  is the salt concentration in moles per liter and  $\kappa_1$  is the measured conductivity and  $\kappa_2$  is the conductivity calculated assuming that no complexing occurred.

### 7.8 Summary of Basic Conductance Formulas

The full conductance approach may be briefly summarized as Equation 7-1

$$\kappa = \sum_i m_i z_i \lambda_i,$$

where  $\lambda$  is given by Equation 7-23

$$\lambda_i = \left( \lambda_i^\circ - \frac{\phi_1 \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right) \left( 1 - \frac{\phi_3 \sqrt{I}}{1 + \phi_2 \sqrt{I}} \right),$$

in which  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are factors dependent primarily on the ion in question but also dependent on the overall ionic nature of the solution and are given by Equations 7-24, 7-26 and 7-29. The terms ultimately required in the equations for  $\phi_2$  and  $\phi_3$  include  $a$ ,  $r^{(o)}$ ,  $r^{(n)}$ ,  $h$ ,  $\mu$ , and  $\omega$ , and they are given by Equations 7-27, 7-36, 7-30, 7-32, 7-33 and 7-34 respectively.

The approximate approach has basically the same application utilizing Equations 7-4 and 7-23 but  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are evaluated with a more liberal interpretation with the effect that  $\lambda$  may be written as Equation 7-41

$$\lambda_i = \left( \lambda_i^\circ - \frac{30.325 z_i \sqrt{I}}{1 + 0.3291 a_i \sqrt{I}} \right) \left( 1 - \frac{0.230 z_i^2 \sqrt{I}}{1 + 0.3291 a_i \sqrt{I}} \right).$$

In all subsequent calculations the approximate form is used. The importance of the conductivity approach used here lies in its ability to be transferred to any stream with any type of ionic composition. Also this method allows for checking analyses without requiring the dilution technique required by Rossum's method (1949).

Deviations between calculated and measured conductivity may be due to a number of factors, all of which are felt to be rarely of major importance in natural waters. They include nonequilibrium conditions in regard to association-dissociation reactions; use of incorrect formation constants; inorganic ions not determined in the analysis; organic or otherwise complexed ions reported without being taken into account in the conductivity calculation; and temperature effects on the dissociation constants being neglected.

The conductance formulas used here have two important applications. One is as a method of checking chemical analyses. The accuracy in this regard seems to be about the same as that of Rossum's method (1949) and does not require any dilution to be performed. The second use, which is what the formulas are used for in this study, is to obtain the specific ion concentrations from conductivity measurements provided the ion proportions are known or adequately predicted.

## Chapter 8 MATHEMATICAL METHODS

A brief presentation is made of the more important basic mathematical methods used in this study for those not familiar with the techniques used.

### 8.1 Least Squares Regression

As the name implies, this is a method by which parameters of a proposed model are estimated such that the fit results in a minimization of the sum of the squared error. Given a dependent variable  $Y$  which is related to an independent variable  $X$  by a model which has  $m$  parameters, we can write

$$Y = f(X; p_1, p_2, \dots, p_m; \epsilon), \quad (8-1)$$

where  $p$  are the parameters to be estimated and  $\epsilon$  is a random component. The random component is the result of stochasticity in the relation between  $X$  and  $Y$ . With the parameters implied and the random component included as a linearly additive error term, Equation 8-1 may be written as

$$Y = f(X) + \epsilon. \quad (8-2)$$

The errors  $e$  between observed values  $y$  of the dependent variable and values computed using the observed values  $x$  of the independent variable are then given by

$$e_i = y_i - f(x_i). \quad (8-3)$$

The sum of the squared errors resulting from  $N$  observations is then given by

$$\sum_{i=1}^N e_i^2 = \sum_{i=1}^N [y_i - f(x_i)]^2. \quad (8-4)$$

To minimize the sum of squared errors with respect to the parameters, the partial derivatives of the sum of squared errors with respect to each of the parameters must equal zero. Thus taking partial derivatives with respect to each of the parameters and setting equal to zero, we obtain  $m$  equations

$$\frac{\partial(e_i^2)}{\partial p_1} = -2 \sum [y_i - f(x_i)] \frac{\partial(f(x_i))}{\partial p_1} = 0 \quad (8-5)$$

⋮  
⋮  
⋮

$$\frac{\partial(e_i^2)}{\partial p_m} = -2 \sum [y_i - f(x_i)] \frac{\partial(f(x_i))}{\partial p_m} = 0,$$

where the summations go over the  $N$  observations.

Solving the  $m$  equations for the  $m$  parameters provides optimal estimates for the parameters with

respect to the least squares criteria. In the general case the parameters are found as roots to Equation 8-5 using a gradient, steepest descent or any other applicable technique. However, in the case of a simple linear function in the parameters, the partial derivatives of the function do not involve the parameters themselves. In this case the solution becomes direct without the need of sequential trial and error approximations. In the case of a simple two parameter linear equation

$$Y = p_1 X + p_2, \quad (8-6)$$

the parameters' estimates are given by

$$\hat{p}_1 = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{N \sum x_i^2 - (\sum x_i)^2}, \quad (8-7)$$

and

$$\hat{p}_2 = \frac{\sum y_i}{N} - \hat{p}_1 \frac{\sum x_i}{N}. \quad (8-8)$$

As an indication of the improvement brought about by the use of the relation, the coefficient of determination  $R^2$  is commonly used.  $R^2$  is simply the ratio of the explained sum of squared error to the total sum of squared error about the mean, or the decimal percent explained variance.

$$R^2 = 1 - \frac{\sum (y_i - f(x_i))^2}{\sum (y_i - \frac{\sum y_i}{N})^2} \quad (8-9)$$

As shown by Equation 8-9  $R^2$  is calculated as one minus the ratio of the residual variance to the total variance. If the sample size is small  $R^2$  as given by Equation 8-8 is positively biased. An unbiased, or adjusted,  $R^2$  may be in this case recommended. For the simple linear case (Equation 8-6), the adjusted  $R^2$  is given by

$$R^2 = 1 - \frac{\sum (y_i - f(x_i))^2}{\sum (y_i - \frac{\sum y_i}{N})^2} \frac{(N-1)}{(N-2)} \quad (8-10)$$

While  $R^2$  indicates the improvement or portion of the variance explained by a particular function or model, another quantity is used to indicate the magnitude of the remaining unaccounted variance. The standard deviation of the residual error,  $\sigma^*$ , is used for this purpose. It is related to  $R^2$  by

$$\sigma^* = \sigma_y \sqrt{(1-R^2)}, \quad (8-11)$$

where  $\sigma_y^2$  is the original variance in the dependent variable. More commonly  $\sigma^*$  is estimated as

$$\hat{\sigma}^* = \sqrt{\frac{\sum (y_i - f(x_i))^2}{D.F.}}, \quad (8-12)$$

where D.F. is the number of degrees of freedom (D.F. equals  $N - 2$  for the simple linear case, Equation 8-6).

Statistical tests and confidence intervals are commonly developed for the simple linear relation under the assumption that the residual errors are estimates of the random component. It is also assumed that the values of the random component are independent and distributed normally about the predicted values with the same variance regardless of the value of the independent variable. Under these assumptions, tests of the slope estimate  $\hat{p}_1$  are based on the statistic

$$T = \frac{(\hat{p}_1 - p_1)}{\hat{\sigma}^*} \sqrt{\frac{N \sum (x_i - \frac{\sum x_i}{N})^2}{\sum x_i^2}}, \quad (8-14)$$

which also is distributed as a Student's  $t$  with  $N-2$  degrees of freedom. In addition, confidence intervals on the estimates for  $\sigma^*$  may be developed using as a pivotal quantity, the statistic

$$T = \frac{(N-2)(\hat{\sigma}^*)^2}{(\sigma^*)^2}, \quad (8-15)$$

having a chi-square distribution with  $n - 2$  degrees of freedom. For more complex models an analysis of variance taking the form of an  $F$ -test may be used. These test statistics are developed under the assumption of serially independent residuals. They may also be used with autocorrelated residuals provided some adjustment is made. Yevjevich (1972a) indicates a method of adjusting parameters for the distributions of the mean and variance through the use of an effective sample size  $N_e$ . The value of  $N_e$  is always less

than the actual sample size. A similar approach may be possible for application to distributions of the test statistics used in Equations 8-13 through 8-15. If no adjustment is made, the effect is to lower the significance level of any test by some unknown amount. That is, if a test is made at the five percent level for the test statistic, the actual significance level being used is somewhat lower, perhaps the ten percent level. Keeping this in mind, any test made without adjustment is valid provided the result is a rejection of the hypothesis of significance. In fact, it is valid at a lower significance level than the nominal level used and as a result is a stronger test for the acceptance of the null hypothesis. On the other hand, tests which result in an acceptance of the significance hypothesis should be interpreted with caution since this test is weakened.

In this study unadjusted tests of significance were used. In testing for significant trends, the hypothesis of the linear trend line slope being different from zero is tested at the nominal five percent

significance level. In all cases the null hypothesis (no significant trend) was accepted.

## 8.2 Weighted Least Squares Regression

Often some observation may be felt to be more or less reliable than the other observations. In these cases it may be justified to assign a weight to each of the observations in an objective manner which reflects the a priori confidence in each observation. The basic approach is the same as for the unweighted least squares regression except that the individual squared errors are multiplied by their respective weights. Thus Equation 8-4 becomes

$$\sum w_i e_i^2 = \sum w_i [y_i - f(x_i)]^2, \quad (8-16)$$

with the summations taken over the  $N$  observations. Taking partials with respect to the  $m$  parameters and setting the resulting equations equal to zero results in  $m$  equations with  $m$  unknown parameters. Solving produces the weighted least square estimates for the parameters. In the case of the simple two parameter linear equation (Equation 8-6) the weighted estimates become

$$\hat{p}_1 = \frac{\sum w_i \sum w_i y_i x_i - \sum w_i x_i \sum w_i y_i}{\sum w_i \sum w_i x_i^2 - (\sum w_i x_i)^2}, \quad (8-17)$$

and

$$\hat{p}_2 = \frac{\sum w_i y_i - \hat{p}_1 \sum w_i x_i}{\sum w_i}, \quad (8-18)$$

as compared with the unweighted estimates given in Equations 8-7 and 8-8. Likewise, weighted estimates of the mean, original variance and residual variance of the dependent variable, and a weighted coefficient of determination may be calculated as follows: the mean of the dependent variable,

$$\hat{\mu}_w = \frac{\sum w_i y_i}{\sum w_i}, \quad (8-19)$$

the variance of the dependent variable,

$$\hat{\sigma}_w^2 = \frac{\sum w_i (y_i - \hat{\mu}_w)^2}{\sum w_i}, \quad (8-20)$$

the unexplained variance,

$$(\hat{\sigma}_w^*)^2 = \frac{\sum w_i (y_i - f(x_i))^2}{\sum w_i}, \quad (8-21)$$

and the coefficient of determination,

$$R_w^2 = 1 - \frac{(\hat{\sigma}_w^*)^2}{\hat{\sigma}_w^2} \quad (8-22)$$

### 8.3 Harmonic Analysis

Due to the annual cycle, periodic terms or parameters having a basic period of one year were expected. Harmonics based on the basic annual period were estimated and removed from many of the parameters where significant. Harmonics based on the other periods such as lunar cycle, weekly cycle or diurnal cycle were not investigated. The basic approach used was Fourier analysis and this is briefly covered in this section.

Consider a parameter  $p$  whose value varies continuously in a periodic manner with a basic cycle of length  $\omega$ . Fourier analysis may then be used to fit the values of  $p$ . Since the values of  $p$  vary with time of year, reference to values at a specific time of the year  $\tau$  will be referred to as  $p_\tau$ .

Fourier analysis involves fitting the values  $p_\tau$  with terms of the form

$$A_j \cos \frac{2\pi j\tau}{\omega} + B_j \sin \frac{2\pi j\tau}{\omega}, \quad (8-23)$$

where  $A_j$  and  $B_j$  are the Fourier coefficients of the  $j$ -th harmonic. Thus  $p$  may be represented at any time within the year as the sum of its annual mean and an infinite number of sine and cosine terms.

$$p_\tau = \bar{p} + \sum_{j=1}^{\infty} [A_j \cos \frac{2\pi j\tau}{\omega} + B_j \sin \frac{2\pi j\tau}{\omega}]. \quad (8-24)$$

Values for the Fourier coefficients may then be found as

$$A_j = \frac{2}{\omega} \int_0^{\omega} p_\tau \cos \frac{2\pi j\tau}{\omega} d\tau, \quad (8-25)$$

and

$$B_j = \frac{2}{\omega} \int_0^{\omega} p_\tau \sin \frac{2\pi j\tau}{\omega} d\tau. \quad (8-26)$$

It is well to note that the coefficient values of terms for one harmonic are not dependent on the coefficient values for the other terms. This fortunate situation will not be true in the next section which covers weighted harmonic analysis.

Unfortunately, the values of  $p$  are not known exactly but must be estimated. Therefore, estimates  $\hat{p}$  of  $p$  must be used in determining harmonics. Also since estimates are made within intervals and experience sampling errors, the coefficients must now be estimated using discrete data. Thus

$$\hat{p}_\tau = p_\tau + \epsilon, \quad (8-27)$$

where  $\hat{p}_\tau$  is the estimate for  $p_\tau$ ,  $\tau$  is now time of year corresponding to the midpoint of the interval, and  $\epsilon$  is the random error in the estimate. Since there are only a finite number of data points to be fit, there is now an upper limit on the number of harmonics which may be fit to the data. The maximum number of harmonics  $m$  is half the number of intervals

$n$  if  $n$  is even and half the number of intervals minus one if  $n$  is odd (Yevjevich, 1972b). In this case the Fourier coefficients are estimated as

$$\hat{A}_j = \frac{2}{\omega} \sum_{k=1}^n \hat{p}_\tau \cos \frac{2\pi j\tau}{\omega}, \quad (8-28)$$

and

$$\hat{B}_j = \frac{2}{\omega} \sum_{k=1}^n \hat{p}_\tau \sin \frac{2\pi j\tau}{\omega}, \quad (8-29)$$

where  $\tau$  is time of year corresponding to the  $k$ -th interval and is given by

$$\tau = \frac{\omega}{n} (k - \frac{1}{2}). \quad (8-30)$$

Since the Fourier coefficients are not determined exactly, but rather estimated with some error, their significance must be determined. Random sampling errors will cause not only the over and under estimation of harmonics actually contained in the population values but also the estimation of harmonics which may not be contained in the population values.

In testing the significance of harmonics, no completely valid method exists. Yevjevich (1972c) discusses several objective and semiobjective approaches, two of which are used here. The first and main approach used is patterned after Fisher's approach. This approach uses the magnitude of the variance of each individual harmonic in testing whether that harmonic is significantly different from what would be expected by pure chance. In testing the largest harmonic (largest in terms of the variance), Fisher's test uses the statistic

$$g = \frac{\hat{c}^2}{2\hat{\sigma}_p^2}, \quad (8-31)$$

where  $\hat{c}^2/2$  is the variance estimate of the largest harmonic and  $\hat{\sigma}_p^2$  is the variance estimate for the  $\hat{p}_\tau$  series. The variance of the harmonics are given by

$$\frac{c_j^2}{2} = \frac{A_j^2}{2} + \frac{B_j^2}{2}. \quad (8-32)$$

The value of  $g$  is then compared with a critical value  $g_c$  which corresponds to the maximum value of  $g$  expected by random chance at a given probability level. Approximate values of  $g_c$  may be calculated by the equation

$$g_c = 1 - \frac{p}{m}, \quad (8-33)$$

where  $p$  is the probability level (usually 0.01 or 0.05) and  $m$  is the maximum number of harmonics. If the largest harmonic is determined to be significant, the next largest is tested. This is repeated until an insignificant harmonic has been tested. In performing these tests, the test statistic is computed as



$$g_j = \frac{\hat{c}_j^2}{2\hat{\sigma}_p^2 - \sum \hat{c}_i^2}, \quad (8-34)$$

where the summation in the denominator is taken over all harmonics of greater magnitude than the harmonic being tested. Yevjevich (1972c) cautions that this approach tends to include more harmonics as significant than it should because of the biases involved.

The second approach used here is to examine the improvement made or variance explained by each harmonic from the largest harmonic to the smallest. This is often done graphically using a cumulative line spectrum or cumulative periodogram. Usually the graph will demonstrate two distinct regions. The first is distinguished by large gains in the cumulative explained variance, indicative of significant harmonics, while the second is typified by slow gradual gains, indicative of periodicity in the sample values due only to chance.

In this study both approaches were used. In no cases were harmonics included which failed Fisher's test. However, harmonics were occasionally rejected although they passed Fisher's test. This was usually where the harmonic in question was the fourth, fifth or sixth significant harmonic and was negligibly small or where its period was less than one tenth of a year. Values used for  $g_c$  were taken at the five percent level (0.044 for one day intervals, and 0.171 for five day intervals).

#### 8.4 Weighted Harmonic Analysis

At times the estimates for the periodic series  $\hat{p}_\tau$  referred to in the last section are not all of equal accuracy. That is, some estimates are more reliable than others. For these cases, it is desirable to weight each estimate and its error by a factor indicating the confidence in the estimate. A logical choice for weights is one over the estimated variance. Using these weights each point is then treated as if it represented  $w$  points where  $w$  is the weight assigned to that point.

In this case, unlike the standard Fourier analysis, the values for the coefficients for the harmonics depend on one another. For this reason, the number of significant harmonics and their periods must be known a priori. The approach taken in this study is to fit the first harmonic, then the first two harmonics together and so on, until the first ten harmonics are fit together. To select the number of significant harmonics, both a modified Fisher's test and a modified periodogram technique are used. A Fisher's  $g$  value is calculated in the same manner as before except the variances are calculated as weighted variances. A weighted  $R^2$  is used in applying the periodogram technique. The calculations for weighted variance and weighted  $R^2$  are covered in Section 8.2.

Since the harmonics can no longer be estimated separately, the procedure is a weighted least squared calculation as presented in Section 8.2. When estimating  $m$  coefficients, the partial differential equations result in  $m$  linear equations in  $m$  unknowns which are easily solved using matrix algebra.

#### 8.5 Bias Correction for Logarithmic Regression

Linear least squares regressions applied to the logarithms of data tend to fit the mean of the logarithms but not the actual means of the data. This bias may be corrected provided reasonable assumptions are made concerning the data. Consider a variable  $Y$  whose logarithms are linearly correlated with the logarithms of a second variable  $X$ . Then using base  $e$  logarithms

$$\ln y_i = a \ln x_i + b + \ln \epsilon_i, \quad (8-35)$$

where  $a$  and  $b$  are parameters and  $\epsilon$  is an error term. If  $\ln \epsilon$  may be considered to be distributed normally about the estimate with a variance of  $\sigma_n^2$ , which is constant and not dependent on  $x$ , the errors  $\epsilon$  are then distributed lognormal. The mean and standard deviation,  $\mu_n$  and  $\sigma_n$ , of a lognormal variable and the mean and standard deviation,  $\mu$  and  $\sigma$ , of that variable's antilogs are related. In this case the moments of  $\epsilon$  are given by (Yevjevich, 1972a)

$$\gamma_r = e^{r\mu_n + r^2 \sigma_n^2 / 2}, \quad (8-36)$$

where  $\gamma_r$  is the  $r$ -th moment of  $\epsilon$  and  $\mu_n$  and  $\sigma_n$  are the mean and standard deviation of  $\ln \epsilon$ . Since  $\ln \epsilon$  is distributed with mean zero and standard deviation  $\sigma_n$ , this reduces to

$$\gamma_r = e^{r^2 \sigma_n^2 / 2}. \quad (8-37)$$

The first moment gives the mean of  $\epsilon$ ,

$$\mu = e^{\sigma_n^2 / 2}, \quad (8-38)$$

or if base ten logarithms are used,

$$\begin{aligned} \mu &= e^{(\sigma_n \ln 10)^2 / 2} \\ &= 10^{1.15 \sigma_n^2}. \end{aligned} \quad (8-39)$$

To determine how to correct for this, Equation 8-35 may be rewritten as

$$y = e^{bX^a} \epsilon. \quad (8-40)$$

Taking expected values

$$E[Y] = e^{bX^a} E[\epsilon], \quad (8-41)$$

or

$$E[Y] = e^{bX^a} e^{\sigma_n^2 / 2}. \quad (8-42)$$

Therefore if an unbiased estimate of  $y$  is desired, the estimate for  $\ln y$  must be increased by  $\sigma_n^2 / 2$  or  $\log y$  by  $1.15 \sigma_n^2$ .

For this study  $\ln \epsilon$  was assumed to be distributed normally, however, similar relationships may be developed by assuming  $\ln \epsilon$  to take on other distributions. For example, by assuming  $\ln \epsilon$  to be of uniform distribution with mean zero and variance  $\sigma_n$ , the mean of  $\epsilon$  is given by

$$\mu = \frac{\sigma_n \sqrt{3} - \sigma_n \sqrt{3}}{\sigma_n \sqrt{12}}, \quad (8-43)$$

which results in bias corrections very near those given for  $\log \epsilon$  normally distributed.

### 8.6 Cross Correlation Analysis

Lag cross correlation is an important tool for investigating the relationship between two time series, particularly when the relationship in time is not already known. This technique is used here to detect if the discharge-concentration relationship could be taken with no lag between the two time series or if significant improvement was possible by lagging one series with respect to the other. The cross correlation coefficients, defined by

$$\rho_k(X,Y) = \frac{\text{cov}(X_i, Y_{i+k})}{(\text{var } X \text{ var } Y)^{1/2}}, \quad (8-44)$$

are estimated and compared with the lag zero correlation. Estimates for  $\rho_k$  are calculated using

$$r_k(X,Y) = \frac{\frac{1}{N} \sum x_i y_{i+k} - \frac{1}{N^2} \sum x_i \sum y_{i+k}}{\left[ \frac{1}{N} \sum x_i^2 - \left( \frac{\sum x_i}{N} \right)^2 \right]^{1/2} \left[ \frac{1}{N} \sum y_{i+k}^2 - \left( \frac{\sum y_{i+k}}{N} \right)^2 \right]^{1/2}} \quad (8-45)$$

where the summations are made over all  $N$  pairs of  $x_i, y_{i+k}$  data.

### 8.7 Autoregressive Models

Often variables have stochastic components which are dependent time series. This is the case found with the stochastic components resulting from the discharge-quality relationships used in this study. Although previous studies have found that the mean and variance of the stochastic components for some hydrologic variables are periodic (Roesner and Yevjevich, 1966), this is not considered necessary for this study. Linear autoregressive models are used in this study. The use of these models is common in hydrology and very well justified by previous applications (Yevjevich, 1972b; Yevjevich, 1972c; Chin and Yevjevich, 1974). The use of first, second and third-order linear autoregressive models is common while the use of higher order models is seldom justified or used in practice. By treating the stochastic component  $\epsilon$  as a linear autoregressive series, the general  $m$ -th order linear autoregressive model may be expressed as

$$\epsilon_i = \sum_{j=1}^m \alpha_j \epsilon_{i-j} + \xi_i, \quad (8-46)$$

in which the  $\alpha$  terms are the population autoregressive coefficients, and  $\xi$  is the linearly independent stochastic component. It should be noted that the values of  $\epsilon$  must be standardized to a mean of zero before the models used here are applicable. The values of the autoregressive coefficients are given directly by the correlation coefficients of the  $\epsilon$  series once the order of the model is selected (Chin and Yevjevich, 1974). For the first-order model

$$\alpha_1 = \rho_1, \quad (8-47)$$

and for the second-order model

$$\alpha_1 = \frac{\rho_1 - \rho_1 \rho_2}{1 - \rho_1^2}, \quad (8-48)$$

and

$$\alpha_2 = \frac{\rho_2 - \rho_1^2}{1 - \rho_1^2}. \quad (8-49)$$

Similar expressions may also be derived for higher order models by considering the relation of the correlation structure to the autoregressive model. Estimates  $\alpha$  for the population autoregressive coefficients are obtained by using the sample correlation coefficient in Equations 8-47 through 8-49. For the first-order model

$$a_1 = r_1. \quad (8-50)$$

For the second-order model

$$a_1 = \frac{r_1 - r_1 r_2}{1 - r_1^2}, \quad (8-51)$$

and

$$a_2 = \frac{r_2 - r_1^2}{1 - r_1^2}. \quad (8-52)$$

The values of the correlation coefficient estimates are given by

$$r_j = \frac{\frac{1}{N} \sum \epsilon_i \epsilon_{i+j} - \frac{1}{N^2} \sum \epsilon_i \sum \epsilon_{i+j}}{\left[ \frac{1}{N} \sum \epsilon_i^2 - \left( \frac{\sum \epsilon_i}{N} \right)^2 \right]^{1/2} \left[ \frac{1}{N} \sum \epsilon_{i+j}^2 - \left( \frac{\sum \epsilon_{i+j}}{N} \right)^2 \right]^{1/2}}, \quad (8-53)$$

where the summations are made over the total number,  $N$ , pairs of  $\epsilon_i$  and  $\epsilon_{i+j}$  data.

The coefficient of determination, which indicates the variance accounted for by the  $m$ -th order linear model is given by

$$R_m^2 = \sum_{j=1}^m \alpha_j \rho_j, \quad (8-54)$$

or may be calculated using the sample estimates

$$R_m^2 = \sum_{j=1}^m a_j r_j . \quad (8-55)$$

Using this, the standard deviation of  $\xi$  is calculated as

$$\sigma_\xi = \sigma_\epsilon \sqrt{1 - R_m^2} . \quad (8-56)$$

For the purposes of this study, the distribution of  $\xi$  is taken to be normal.

Yevjevich (1972c) proposed a simplified method for determining the order of the linear autoregressive model. The criteria for selection is the successive amounts of improvement as measured by  $R_m^2$  brought about by the linear model. By examining the changes in the explained variance in  $\epsilon$  from one model to the next, the order of the model may be objectively selected. If the change in the  $R^2$  values from one model to the next higher model is greater than a pre-selected value,  $\Delta R^2$ , the next higher model is selected. If the improvement is less than  $\Delta R^2$ , the higher model is rejected. Values for  $\Delta R^2$  are recommended to be 0.01 or 0.02 or a similar small difference. For this study 0.02 was selected when using this method.

## 8.8 Normal Independent Stochastic Components

The independent stochastic component  $\xi$  is obtained after removing the autoregressive tendencies from the stochastic component  $\epsilon$ . Throughout this study the  $\xi$  series are assumed to be normally distributed. This is felt to be a reasonable assumption and further investigation into the structure of the  $\xi$  distribution is not justified. The probability density function for the normal distribution is taken to be given by

$$f(\xi) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2} (\xi-\mu)^2\right] , \quad (8-57)$$

where  $\mu$  and  $\sigma$  are the mean and standard deviation of  $\xi$ .

## 8.9 Leap Year Effect

So that all years would have an equal number of days, one day is eliminated from each leap year. The day selected for elimination is leap year day itself, February 29. This shift in the data does not significantly affect the results, but greatly facilitates calculations, particularly of periodic components. However, if study were to be made of periodicities resulting from man's activities having a basic period of one calendar week this procedure could not be used. In this case, the day of the week would be of importance and would have to be preserved.

Chapter 9  
DETERMINISTIC MODEL OF ION CONCENTRATION PREDICITON

Predicted ion concentrations are generated on a daily basis using the deterministic components of the relationships derived. A comparison is made between the observed and predicted values.

9.1 Application of the Model

The application of the complete model for predicting ion concentrations from flow records consists of three steps: prediction of the conductivity, prediction of the ion proportions, and the determination of the proper total concentration (also specific ion concentrations) for the predicted conductivity.

The conductivity is predicted by Equation 5-36,

$$\log \kappa = a_{\tau}(\log Q - c_1) + c_2 + d_{\tau} .$$

A correction for the bias introduced by using logarithms is applied, which amounts to  $1.15(\sigma)^2$  being added to the value given by the above equation for the  $\log \kappa$ . This bias correction, as discussed in Chapter 8, is based on the assumption of lognormally distributed residuals. The correction is small in this case, and could be ignored with negligible effect.

Proportions of the ions are predicted under the assumption of a log-linear relation with the flow (Equation 6-5), a semilog-linear relation with the flow, (Equation 6-5) or as a constant relation (Equation 6-6). The relations used for the various ions are shown in Table 6-2. Again a bias correction is made when using the log-linear relations. For some of the minor ions this correction is substantial.

Once both the ion proportions and the conductivity have been predicted, all that remains is to determine the proper total concentration. This concentration is determined by a trial-and-error procedure. First, an initial value for the total concentration,  $C_T$  in meq/l, is determined by

$$C_T = 0.0115 \kappa_{\text{pred}} . \quad (9-1) \quad (9-1)$$

Using this approximate total concentration with the predicted ion proportions, the specific ion concentrations can be calculated. The conductivity is then calculated by using these approximate concentrations. The procedure for making this calculation is covered in Chapter 7. A new approximation for the proper total concentration is obtained by a simple linear interpolation using the predicted conductivity and the value just calculated.

$$C_T = \frac{\kappa_{\text{pred}} C_T'}{\kappa_{\text{calc}}} , \quad (9-2)$$

where the new estimate for the total concentration is  $C_T$ , the old estimate is  $C_T'$ , the calculated conductivity using  $C_T'$  is  $\kappa_{\text{calc}}$  and  $\kappa_{\text{pred}}$  is the predicted conductivity. It was generally found that this procedure takes three iterations to arrive at a value for the concentration which when used to calculate the

conductivity checks to within 0.5 percent of the actual conductivity.

9.2 Comparison with Measured Data

Figures 9-1 and 9-2 show the predicted and observed conductance values for the two years of the Henry's Fork River data which were not used in the model determinations. The explained variance for these two years of data is 84 percent.

Conductivity,  $\mu\text{U}/\text{cm}$

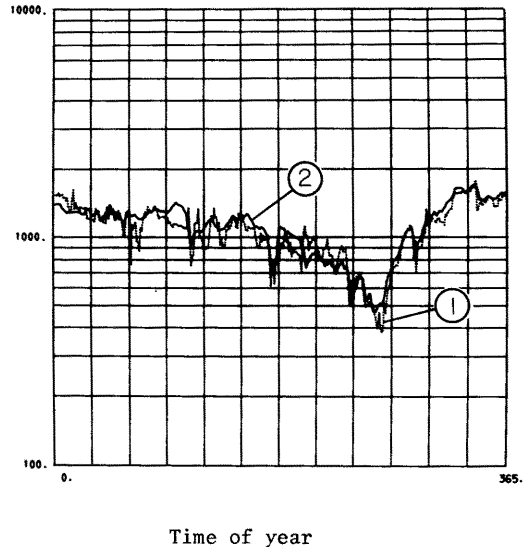


Figure 9-1. Measured (1) and predicted (2) conductivity of the Henry's Fork River for the water year beginning October 1, 1970.

Conductivity,  $\mu\text{U}/\text{cm}$

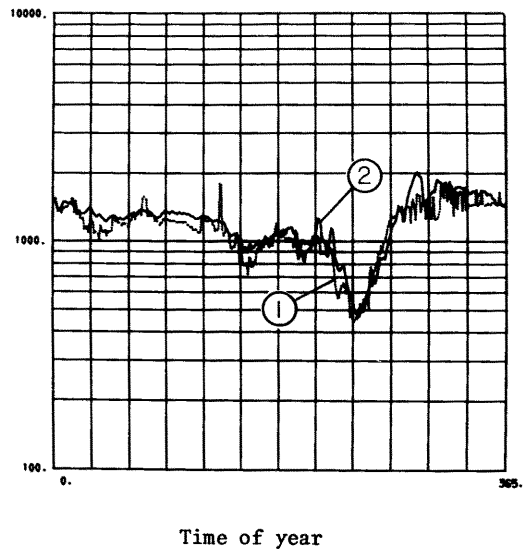


Figure 9-2. Measured (1) and predicted (2) conductivity of the Henry's Fork River for the water year beginning October 1, 1970.

During these same two years, twenty-four chemical samples were taken and analyzed by the U.S. Geological Survey. The results of these analyses and the results of predicting the same concentrations are shown in Table 9-1. Generally the results are excellent with the possible exception of the nitrate and the pH. Both of these showed a large unexplained variance in their proportions. It should be noted that the predicted values were obtained using the mean daily flow rather than the instantaneous flow corresponding to the actual chemical analysis. This difference may in some cases explain a portion of the discrepancies between the observed and predicted concentrations.

Table A9-1 of the Appendix shows daily ion concentrations predicted for 1970 for the Henry's Fork River.

### 9.3 Closing Remarks

It can be concluded that the predicted concentrations may for some purposes be used as if they were observed chemical analyses. While differences do

exist, in practical application they are small compared to the total variation in the concentrations. There are four major advantages in using the predicted values over the observed values. First, they are easier to obtain. Second, they may be calculated using the mean daily flow and thus represent the average daily values rather than instantaneous or composite instantaneous values. This would tend to make possible a more accurate calculation of the salt load of a stream. Third, the results are always complete with no partial samples as is the most prevalent case for chemical analyses. Fourth, the fact that data may be predicted for any desired time interval is a considerable advantage over the irregular spacing typical of chemical analyses.

Modifications to this approach provide additional flexibility. Conductivity could easily be observed leaving only the ion proportions to be predicted. Also, those constituents which are not well predicted could be determined by chemical analyses. This would result in highly accurate data with a minimum of sampling.

Table 9-1. Comparison of measured and predicted chemical constituents of the Henry's Fork River, for the water years beginning October 1, 1970 and 1971.

Date	Daily Mean Flow	Instantaneous Flow	Conductivity $\mu\text{U/cm}$	Concentrations in parts per million												Remarks	
				Ca	Mg	Na	K	Fe	pH	$\text{HCO}_3$	$\text{SO}_4$	Cl	F	$\text{NO}_3$	B		$\text{SiO}_2$
10/8/70	62	61	1460	8.0	6.7	2.6	.28	.0025	8.3	4.7	13.	.59	.026	.0016	.024	.40	measured
			1336	7.5	5.5	2.5	.27	.0033	7.9	5.2	9.9	.69	.038	.018	.022	.42	predicted
11/5/70	81	82	1410	8.0	6.6	2.3	.21	.0029	8.1	4.7	12.	.62	.026	.0016	.013	.33	measured
			1263	7.2	5.1	2.3	.26	.0033	7.9	5.1	9.1	.64	.037	.017	.021	.41	predicted
12/2/70	74	74	1290	7.0	5.8	2.2	.19	.00036	8.4	4.5	10.	.54	.021	.0016	.015	.32	measured
			1243	7.0	5.1	2.3	.25	.0032	7.9	4.9	9.0	.63	.036	.017	.020	.40	predicted
1/11/71	34	34	1260	6.5	4.7	1.7	1.6	.00072	8.5	4.3	8.5	.45	.021	.0065	.015	.27	measured
			1383	7.7	5.8	2.7	.26	.0028	7.9	4.9	11.	.74	.035	.019	.023	.41	predicted
2/3/71	58	58	1010	6.0	4.0	1.8	.18	.0050	8.5	4.1	7.5	.42	.021	.0065	.014	.27	measured
			1194	6.6	4.9	2.2	.23	.0028	7.9	4.5	8.8	.61	.033	.016	.019	.37	predicted
3/6/71	33	33	1100	3.4	0	1.9	.17	.00036	8.5	4.2	9.2	.82	.032	.0032	.013	.30	measured
			1270	7.0	5.3	2.5	.24	.0025	8.0	4.4	9.8	.67	.031	.017	.021	.37	predicted
4/7/71	82	73	946	5.5	4.3	1.9	.18	.0011	8.5	4.0	6.7	.51	.032	.0032	.012	.28	measured
			1042	5.8	4.1	1.9	.21	.0027	8.0	4.1	7.3	.51	.030	.014	.016	.33	predicted
5/7/71	156	142	790	4.7	3.5	1.5	.16	0	8.6	3.7	5.6	.45	.026	.0032	.012	.27	measured
			782	4.3	2.9	1.3	.16	.0024	8.0	3.3	5.0	.36	.025	.0098	.012	.26	predicted
6/3/71	310	254	627	3.7	2.4	.96	.14	.0032	8.4	3.1	3.7	.22	.021	.0065	.0083	.28	measured
			622	3.4	2.2	.96	.13	.0023	8.1	2.8	3.6	.27	.022	.0074	.0092	.22	predicted
7/9/71	128	118	941	5.5	3.5	1.3	.18	.0011	8.6	4.4	6.0	.28	0	.014	.37	measured	
			934	5.2	3.6	1.6	.19	.0027	8.0	3.9	6.2	.44	.029	.012	.015	.31	predicted
8/7/71	37	33	1110	6.0	5.0	2.1	.23	.00072	8.3	4.3	8.7	.45	.016	.021	.38	measured	
			1277	7.0	5.3	2.5	.24	.0026	7.9	4.6	9.8	.67	.032	.017	.021	.37	predicted
9/2/71	6	5	1670	9.5	7.3	3.2	.28	.0029	8.1	5.4	14.	.73	.053	.031	.45	measured	
			1667	8.9	7.5	3.8	.28	.0020	8.0	4.6	15.	.93	.030	.023	.028	.40	predicted
10/8/71	35	36	1430	7.5	6.5	2.5	.24	.0036	8.7	4.6	12.	.48	.037	.022	.37	measured	
			1464	8.3	6.2	2.9	.28	.0030	7.9	5.3	12.	.79	.037	.020	.024	.44	predicted
11/12/71	90	99	1100	6.0	4.5	1.9	.21	.00072	8.4	4.3	7.9	.39	.021	.016	.33	measured	
			1224	6.9	5.0	2.2	.25	.0033	7.9	5.0	8.7	.61	.037	.016	.020	.41	predicted
12/4/71	51	51	1340	7.5	6.1	2.3	.23	.00072	8.3	5.1	10.	.56	.026	.019	.37	measured	
			1342	7.5	5.6	2.6	.26	.0031	7.9	5.1	10.	.70	.036	.018	.022	.42	predicted
1/19/72	43	43	1140	7.0	5.1	1.8	.28	.0014	8.0	4.8	9.0	.48	.0053	.016	.32	measured	
			1302	7.2	5.4	2.5	.25	.0028	7.9	4.8	9.9	.68	.034	.018	.021	.39	predicted
2/6/72	46	46	1160						8.1							measured	
			1233	6.8	5.1	2.4	.24	.0027	7.9	4.5	9.2	.64	.032	.017	.020	.37	predicted
3/3/72	247	243	770	4.1	2.4	1.5	.20	.0014	8.3	3.4	4.8	.34	.016	.010	.25	measured	
			894	5.0	3.4	1.5	.19	.0032	7.9	4.1	5.6	.41	.031	.011	.014	.35	predicted
4/4/72	62	55	1040	6.0	4.4	1.8	.18	.00036	8.4	4.7	7.3	.48	.021	.015	.28	measured	
			1117	6.2	4.5	2.1	.22	.0027	8.0	4.2	8.1	.56	.031	.015	.018	.35	predicted
5/17/72	102	102	676	3.8	2.5	1.0	.15	.0014	8.5	3.2	4.0	.28	.016	.012	.25	measured	
			850	4.6	3.3	1.5	.17	.0023	8.0	3.4	5.7	.49	.025	.011	.013	.27	predicted
6/15/72	291	295	730	3.9	2.6	.91	.14	.0029	8.3	3.6	4.2	.24	.021	.012	.30	measured	
			664	3.6	2.4	1.0	.14	.0024	8.1	3.0	3.9	.29	.023	.0080	.0099	.24	predicted
7/11/72	35	33	1310	8.0	5.7	2.6	.27	.0021	8.9	4.9	11.	.59	.032	.021	.52	measured	
			1223	6.7	5.0	2.4	.23	.0024	8.0	4.3	9.3	.64	.030	.016	.020	.35	predicted
8/2/72	7	3	1800	9.5	8.2	3.5	.31	.0021	8.7	4.9	17.	.82	.042	.033	.38	measured	
			1624	8.7	7.3	3.6	.27	.0020	8.0	4.6	14.	.95	.030	.023	.027	.39	predicted
9/8/72	9	10	1710	10.	8.2	3.2	.31	.0029	8.1	4.6	16.	.79	.037	.028	.40	measured	
			1608	8.7	7.1	3.5	.28	.0022	8.0	4.7	14.	.93	.031	.022	.027	.40	predicted

## Chapter 10 STOCHASTIC MODEL

By adding the stochastic components to the basic deterministic relationships, simulation of daily conductivity data is made more complete. Simulation in this manner tends to preserve the statistical properties found in the original series. Values obtained by this procedure should not be used for prediction purposes, however, since the values obtained may fluctuate widely from their expected values due to the stochastic components.

### 10.1 Addition of Stochastic Components

A stochastic component is added to the conductivity series as described in Chapter 5. First, a normal independent stochastic series is generated ( $\xi$ ) with mean zero and variance as given in Table 5-14. Next, the first-order autoregressive model is applied according to Equation 5-39 as

$$\epsilon_i = a \xi_{i-1} + \xi_i .$$

This stochastic component is added to the predicted log of the conductivity series. It should be noted that in this case no correction for bias is applied. Also the distribution of the stochastic component is assumed to be normal for this study. While this is felt to be a fair assumption, no attempt has been made to verify it.

Stochastic components could not be determined for the ion proportions due to the composite nature of the data. Therefore, simulation of the individual concentrations will not be done.

### 10.2 Results

One complete year of daily conductivity data has been simulated for the year 1970 on the Henry's Fork River. Results are contained in Table A10-1 of the Appendix along with the predicted and measured values for that year. This is the same year and stream used in Chapter 9 to illustrate the generation of predicted data for both conductivity and individual constituent concentrations. The results of that prediction are shown in Table A9-1 of the Appendix.

### 10.3 Closing Remarks

Simulation tends to produce a more representative series and should be used wherever the population characteristics need to be preserved, particularly in the study of the distribution of rare occurrences, runs or ranges. On the other hand, the increased complexity, both in model parameter estimation and in generation is not needed if only estimates are required.

## Chapter 11 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

### 11.1 Summary

A mathematical procedure for extracting inorganic water quality information from flow records has been developed and applied to five natural streams. The streams are the Henry's Fork River, the New Fork River, the Saline River, the Pecos River and the Wind River. The method relies on three basic principles: (1) the total concentration of inorganics as represented by the conductivity is highly related to hydrologic variables; (2) the ion proportions are near constant or adequately related to the discharge; and (3) the ion concentrations are deterministically related to the conductivity.

Conductivity measurements were fit with a linear logarithmic relation with discharge. The inclusion of a periodic intercept term, accounting for annual variations in the relationship, was justified. Although the model parameters vary greatly from stream to stream, the basic model is felt to be generally applicable to natural streams. For the five streams studied, between 76 and 84 percent of the variance in the logarithm of the conductivity was explained by this model. The inclusion of both periodic slope and periodic intercept increases the explained variance to between 81 and 87 percent. The residuals resulting from the modeling are found to be highly autoregressive. A first-order autoregressive model is used for four of the five streams, while a second-order autoregressive model is used for the New Fork River.

Thirteen inorganic constituents are investigated. These include the seven major ions found in natural waters: calcium, magnesium, sodium, potassium, bicarbonate, sulfate and chloride. The six other constituents studied are hydrogen ion, iron, fluoride, boron, nitrate and silica. Ion proportions are relatively constant on four of the five streams studied. Although variations in ion proportions for these streams are small, they can be related to discharge. Ion proportions vary widely on the Saline River and are distinctly related to the stream discharge. Both logarithmic, semilogarithmic and constant relations are used to predict the ion proportions. The results are good although considerable variation in the minor ions could not be explained.

A deterministic model relating conductivity to the specific ion concentrations was developed as a direct result of the application of a previously developed theory. Both a theoretical equation and a simplified equation are presented. The simplified equation performs as well as the theoretical equation except for solutions of unusually high concentration. An accuracy of plus or minus one percent is estimated for concentrations of less than 1,000 ppm with the simplified equation. In application to 784 samples, the percent differences observed had a mean of 0.68 percent and standard deviation of 3.4 percent. These differences are of the same magnitude as the accuracy of the conductivity measurement process.

The models developed have been used together to both predict and simulate inorganic water quality data from discharge measurements on the Henry's Fork River for the water years beginning October 1, 1970 and 1971. The conductivity data for these two years was not used in estimating model parameters. A comparison

is made between predicted ion concentrations and actual chemical analyses performed during the two year period in Table 9-1. For one complete year, the ion concentrations are predicted on a daily basis and are shown in Table A9-1 of the Appendix. Simulated, predicted and measured values for conductivity for the same year are shown in Table A10-1 of the Appendix.

### 11.2 Comparison with Past Studies

A brief review of what has typically been done in relating inorganic water quality to stream discharge is in order. Most studies have dealt with only one stream and only one relationship between quality and discharge. No relationship has been adopted for general use. The specific constituents considered in most cases are very limited, with most studies concentrating on only one variable such as total dissolved solids. Only a few studies have made use of conductivity data although conductivity data are much easier to obtain than chemical analysis data and are usually on a daily basis. In all cases, the studies which have related ion concentrations to conductivity have used empirical relationships which must be derived for each individual stream. The prediction of complete chemical analyses has not been previously done. The time intervals have varied considerably; annual and monthly values are often used.

This study has endeavored both to improve over past studies and to make efficient use of the commonly available data. Conductivity is used as an indicator of the total inorganic dissolved solids. In this way the most variable and important quantity, the total concentration, is modeled using a great deal of daily conductivity data. This also allowed an analysis of the stochastic behavior of this important variable.

The proportions of the various inorganic constituents on most streams are found to vary only slightly. For this reason, the proportions rather than the actual constituent concentrations were related to discharge. The highly variable total concentration is modeled by using daily conductivity data. The relatively constant constituent proportions are modeled using the very limited number of irregularly spaced chemical analyses. In this manner efficient use is made of the available data.

A theoretically based method for relating ion concentrations to conductivity is developed and applied in this study. Unlike empirical relations between conductivity and ion concentrations previously used, this approach may be applied to any natural water sample and need not be determined separately for each individual stream. This method also provides an additional way of checking chemical analyses for incompleteness or inaccuracies.

A number of potential relationships were considered for the conductivity-discharge model. It was found that the simple relation adopted performed equally well as compared with more complex relationships. Five streams were studied using the same model and similar results were obtained with each stream. Although rejected as being too complex to be practical, a physically based model was developed in some detail.

### 11.3 Conclusions

Although numerous studies have been made previously concerning the relationship between inorganic water quality and stream discharge, this work has further improved the knowledge of the relationship. It may be concluded that the methods used in this study show promise of being generally applicable to natural streams. The approach taken makes efficient use of the data presently available. The mathematical models developed in this study may be used for two purposes: (1) extracting additional water quality information from past records, and (2) predicting inorganic water quality without actual chemical analyses.

Past flow records are seldom used to expand the knowledge of the water quality for a given stream. The model makes this possible once the parameters are specified. Perhaps of more importance, conductivity records which had been used only as a rough indication of inorganic concentrations may be used to accurately estimate actual inorganic constituent concentrations. In this case, the only required estimates are the ion proportions. Since conductivity records are more plentiful than chemical analyses data, the benefits of the deterministic relation between conductivity and specific ion concentration are substantial.

Present chemical records are often of little value or are difficult to use due to undetermined constituents, gaps and irregular spacing of the composite samples. All of these problems are eliminated through the use of models developed in this study. Future sampling could be reduced to those constituents not adequately defined by the modeling process.

### 11.4 Recommendations for Future Research

Starting with the results obtained in this study significant areas for future research in refining, improving or interpreting the quality models are available. In applying the models to streams having more diversity, the models may be further verified or modified.

In order that simulation of inorganic constituents may be made, further study is required regarding the stochastic behavior of the ion proportions.

A more intensive study of antecedent effects and their removal is justified. The models developed could also be expanded to be applicable to streams subject to well defined influences from man's activities. This could be done by separating man's effects or modifying the entire model. It is expected that a weekly periodicity would be observed which warrants modeling. Diurnal variations provide another area in which research is possible.

Studies involving the interrelation of models for various streams within a basin or within nearby basins are needed. The transfer of information from one basin or stream to another may greatly increase the value of present discharge and quality data. Similar studies of a basin where two streams merge to form a third would provide valuable insight into how the model parameters are influenced.

Information on the value of data obtained by the models is lacking. The conditions under which data obtained through the application of these relationships may be used have not been specified and justification for the use of these data in place of actual chemical analyses in the future has not been made. These topics deserve additional study. Knowledge is also lacking of the proper frequency of reporting generated data, the amount and frequency of measured data required to efficiently estimate the parameters, and ways of determining the economic advantage of generating data.

Approaches similar to those used here could be applied to nonconservative and/or organic constituents although the relations would probably not be as accurate. Possible application could be made with chemical oxygen demand (COD), total organic carbon (TOC), dissolved oxygen (DO), biochemical oxygen demand (BOD), and various nutrients and trace constituents such as heavy metals or radioactive materials.



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APPENDIX A

Table A4-1. Typical chemical analysis data for the five streams studied.

(Concentrations in Parts Per Million)															
Date of Collection	Mean Discharge	Silica (SiO <sub>2</sub> )	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Fluoride (F)	Nitrate (NO <sub>3</sub> )	Boron (B)	Specific Conductance (μ U at 25°C)	pH
<b>Henry's Fork River at Linwood, Utah</b>															
Oct. 21-31, 1954	10.3	23	--	198	105	108	12	302	815	53	--	0.3	0.37	1,870	7.9
Jan. 11-20, 1955	25.0	23	--	149	70	69	8.5	270	523	55	--	1.2	0.17	1,360	7.7
Apr. 11-20, 1955	70.0	23	--	100	45	50	8.9	243	305	27	--	1.8	0.14	979	7.7
June 21-30, 1955	31.4	26	--	150	73	88	9.7	294	545	35	--	4.8	0.23	1,430	7.8
Sept. 1-10, 1955	1.7	26	--	324	161	205	14	337	1,470	84	--	6.2	0.74	2,880	8.0
<b>New Fork River near Big Piney, Wyoming</b>															
Dec. 1-31, 1966	219	11	--	30	5.8	11	1.4	128	16	2.8	0.4	0.1	0.05	267	7.9
Mar. 15-31, 1967	229	8.5	--	25	4.3	12	1.8	104	13	5.0	0.2	0.2	0.02	209	7.7
June 1-10, 1967	3,378	5.4	--	9.8	1.1	2.1	0.8	36	3.3	2.1	0.2	0.0	0.02	76	7.1
July 16-31, 1967	1,896	7.3	--	14	5.8	4.6	2.5	71	9.9	1.8	0.2	0.5	0.04	132	7.0
Sept. 1-12, 1967	342	10	--	27	4.9	9.1	2.0	110	12	1.8	0.3	0.0	0.03	207	7.8
<b>Pecos River at Puerto de Luna, New Mexico</b>															
Oct. 6-7, 1954	11,050	18	--	81	10	(Na+K = 10)	--	172	113	5.0	--	0.2	--	478	7.7
Nov. 11-20, 1954	98.4	17	--	560	90	112	--	185	1,600	165	--	0.5	--	2,960	7.8
May 24-31, 1955	253	15	--	183	27	32	--	146	444	43	--	2.2	--	1,120	7.7
July 11-15, 1955	63.8	23	--	596	88	108	--	137	1,670	146	--	0.5	--	2,975	7.9
Aug. 12-15, 1955	685	15	--	214	28	35	--	164	499	46	--	1.5	--	1,230	7.4
<b>Saline River near Russell, Kansas</b>															
Nov. 8, 1962	70	17	0.04	162	39	221	15	242	358	353	0.5	0.4	0.21	2,130	7.9
Feb. 8, 1963	139	14	0.07	126	29	112	9.4	324	255	181	0.5	3.6	0.16	1,380	7.7
April 9, 1963	51	10	0.10	140	42	237	17	185	570	376	0.6	0.4	0.21	2,190	7.8
July 9, 1963	15	20	0.02	157	54	532	22	232	474	790	0.7	0.4	0.42	3,760	7.6
Aug. 23, 1963	7.0	15	0.03	177	69	836	25	254	615	1,215	0.7	0.8	0.50	5,300	7.6
<b>Wind River at Riverton, Wyoming</b>															
Nov. 4-16, 1965	529	14	--	44	16	24	2.8	165	88	5.3	0.4	0.0	0.09	455	7.6
Jan. 16-31, 1966	414	15	--	46	18	28	3.3	183	87	5.3	0.3	0.7	0.04	474	7.9
May 8-14, 1966	533	15	--	34	14	26	1.4	155	60	4.6	0.3	0.2	0.11	386	7.2
June 11-19, 1966	1,253	15	--	24	8.9	12	1.7	113	31	1.8	0.3	0.5	0.02	253	7.4
Sept. 15-30, 1966	308	16	--	49	7.9	43	2.9	179	95	5.3	0.4	0.0	0.06	470	7.8

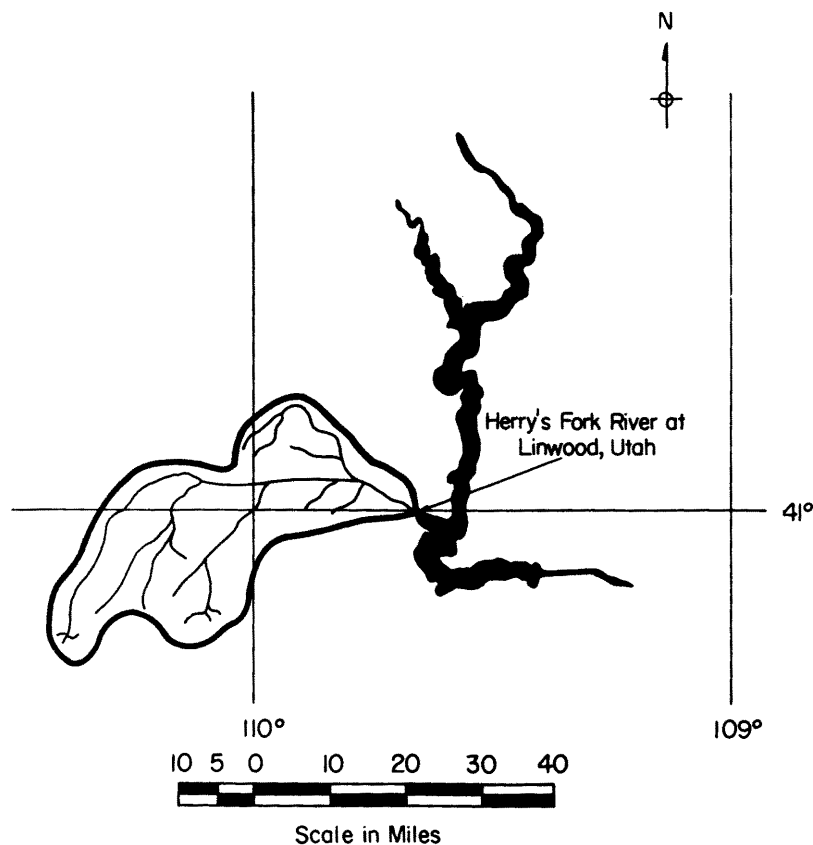


Figure A4-1. Henry's Fork River Drainage.

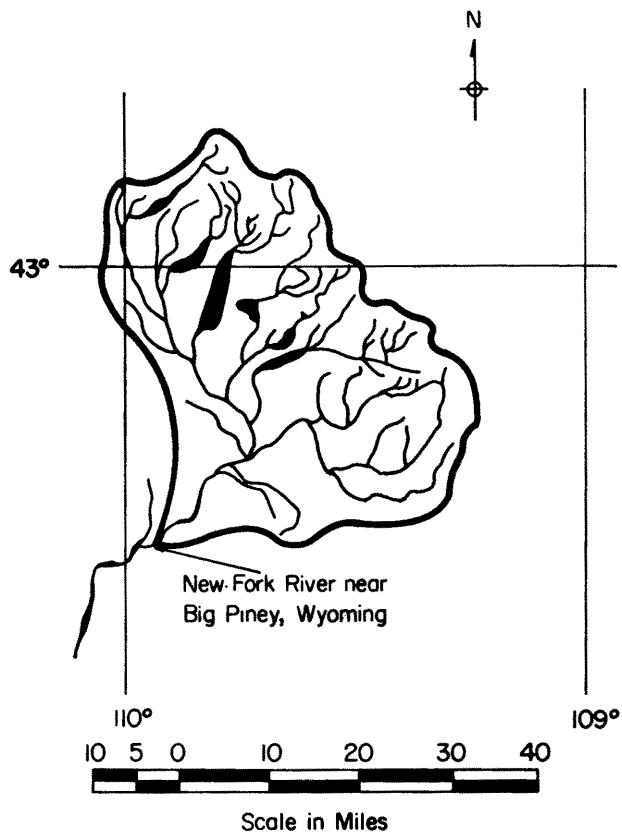


Figure A4-2. New Fork River Drainage.

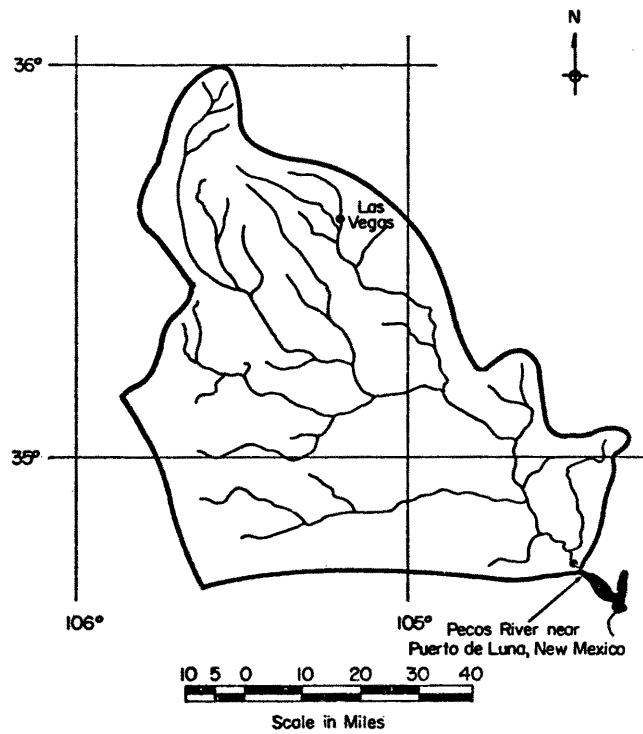


Figure A4-3. Pecos River Drainage.

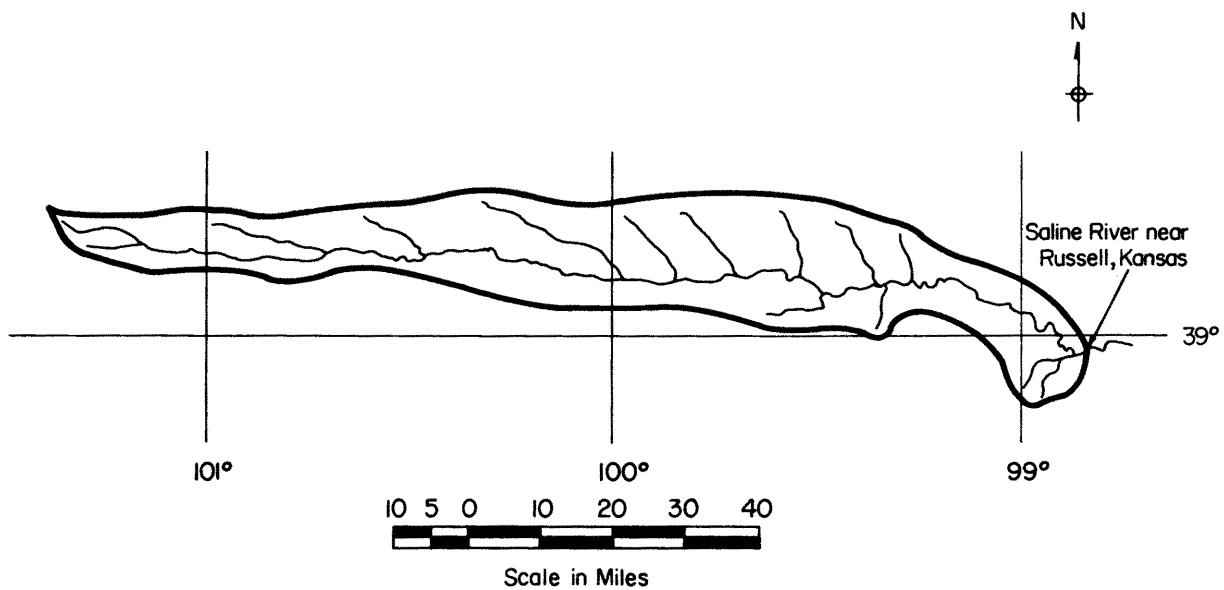


Figure A4-4. Saline River Drainage.

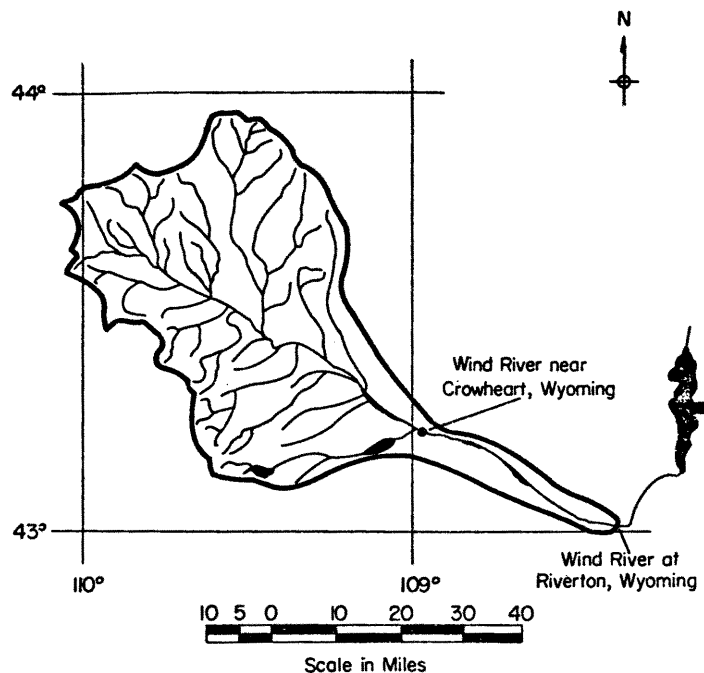


Figure A4-5. Wind River Drainage.

Table A7-1. Equivalent Conductances of some electrolytes in aqueous solutions at 25°C.

Compound	Infinite dilution	Concentrations in gram equivalents per 1000 cm <sup>3</sup>						
		0.0005	0.001	0.005	0.01	0.02	0.05	0.1
(Equivalent Conductances in mhos-cm <sup>2</sup> per equivalent)								
AgNO <sub>3</sub>	133.36	131.36	130.51	127.20	124.76	121.41	115.24	109.14
BaCl <sub>2</sub>	139.98	135.96	134.34	128.02	123.94	119.09	111.48	105.19
CaCl <sub>2</sub>	135.84	131.93	130.36	124.25	120.36	115.65	108.46	102.4
Ca(OH) <sub>2</sub>	257.9			232.9	225.9	213.9		
CaSO <sub>4</sub>	133.6	121.6	115.26	94.07	83.12	72.20	59.05	50.58
HCl	426.16	422.74	421.36	415.80	412.00	407.24	399.09	391.32
KBr	151.9			146.09	143.43	140.48	135.68	131.39
KCl	149.86	147.81	146.95	143.35	141.27	138.34	133.37	128.96
KClO <sub>4</sub>	140.04	138.76	137.87	134.16	131.46	137.92	121.72	115.20
K <sub>3</sub> Fe(CN) <sub>6</sub>	174.5	166.4	163.1	150.7				
K <sub>4</sub> Fe(CN) <sub>6</sub>	184.5		167.24	146.09	134.83	122.82	107.70	97.87
KHCO <sub>3</sub>	118.0	116.10	115.34	112.24	110.08	107.22		
KI	150.38			144.37	142.18	139.45	134.97	131.11
KIO <sub>4</sub>	127.92	125.80	124.94	121.24	118.51	114.14	106.72	98.12
KNO <sub>3</sub>	114.96	142.77	141.84	138.48	132.82	132.41	126.31	120.40
KReO <sub>4</sub>	128.20	126.05	125.12	121.31	118.49	114.49	106.40	97.40
LaCl <sub>3</sub>	145.8	139.6	137.0	127.5	121.8	115.3	106.2	99.1
LiCl	115.05	113.15	112.40	109.40	107.40	104.65	100.11	95.86
LiClO <sub>4</sub>	105.98	104.18	103.44	100.57	98.61	96.18	92.20	88.56
MgCl <sub>2</sub>	129.40	125.61	124.11	118.31	114.55	110.04	103.08	97.10
NH <sub>4</sub> Cl	149.7			146.8	143.5	141.28	138.33	133.29
NaCl	126.45	124.50	123.74	120.65	118.51	115.51	111.06	106.74
NaClO <sub>4</sub>	117.48	115.64	114.87	111.75	109.51	106.96	102.40	98.43
NaI	126.94	125.36	124.25	121.25	119.24	116.70	112.79	108.78
NaOOCCH <sub>3</sub>	91.0	89.2	88.5	85.72	83.76	81.24	76.92	72.80
NaOOC <sub>2</sub> H <sub>5</sub>	85.9		83.5	80.9	79.1	76.6		
NaOOC <sub>3</sub> H <sub>7</sub>	82.70	81.04	80.31	77.58	75.76	73.39	69.32	65.27
NaOH	247.8	245.6	244.7	240.8	238.0			
Na <sub>2</sub> SO <sub>4</sub>	129.9	125.74	124.15	117.15	112.44	106.78	97.75	89.98
SrCl <sub>2</sub>	135.80	131.90	130.33	124.24	120.24	115.54	108.25	102.19
ZnSO <sub>4</sub>	132.8	121.4	114.53	95.49	84.91	74.24	61.20	52.64

(Chemical Rubber Company, 1964)

Table A7-2. Properties of ion species common in natural waters.

Ion	Size Parameter <sup>1</sup> a	Charge and sign sz	Molecular <sup>2</sup> weight	Limiting Equivalent <sup>3</sup> Conductivity $\lambda^\circ$
<u>Positive Ions</u>				
H <sup>+</sup>	9	+1	1.00797	349.81
Na <sup>+</sup>	4-4.5	+1	22.9898	50.10
K <sup>+</sup>	3	+1	39.1020	73.50
Fe <sup>++</sup> (complexed)	4*	+2*	55.8470	100.0*
Mn <sup>++</sup>	6	+2	54.9340	42.0*
Ca <sup>++</sup>	6	+2	40.0800	59.50
CaHCO <sub>3</sub> <sup>+</sup>	3*	+1	101.0973	70.0*
CaOH <sup>+</sup>	3*	+1	57.0874	70.0*
Mg <sup>++</sup>	8	+2	24.3120	53.05
MgHCO <sub>3</sub> <sup>+</sup>	3*	+1	85.3293	70.0*
MgOH <sup>+</sup>	3*	+1	41.3194	70.0*
<u>Negative Ions</u>				
OH <sup>-</sup>	3.5	-1	17.0074	199.18
Cl <sup>-</sup>	3	-1	35.4530	76.35
F <sup>-</sup>	3.5	-1	18.9984	55.4
NO <sub>3</sub> <sup>-</sup>	3.0	-1	62.0049	71.46
HCO <sub>3</sub> <sup>-</sup>	4.0-4.5	-1	61.0173	44.50
NaSO <sub>4</sub> <sup>-</sup>	3*	-1	119.0518	70.0*
KSO <sub>4</sub> <sup>-</sup>	3*	-1	135.1640	70.0*
HSO <sub>4</sub> <sup>-</sup>	4*	-1	97.0700	70.0*
SO <sub>4</sub> <sup>-2</sup>	4.0-4.5	-2	96.0620	80.02
CO <sub>3</sub> <sup>-2</sup>	4.5	-2	60.0094	69.3
NaCO <sub>3</sub> <sup>-</sup>	3*	-1	89.9992	70.0*
<u>Uncharged Complex Species</u>				
B (complexed)			10.8110	
CaSO <sub>4</sub>			136.1420	
MgSO <sub>4</sub>			120.3740	
NaHCO <sub>3</sub>			84.0071	
CaCO <sub>3</sub>			100.0894	
MgCO <sub>3</sub>			84.3214	
H <sub>2</sub> CO <sub>3</sub>			62.0253	
NaOH			39.9972	
SiO <sub>2</sub>			60.0850	

\* Indicates values for which data was not available and which were estimated for use in this study by consideration of diffusion data, if available, or by consideration of  $\lambda^\circ$  values for other species involving similar ions or ion radicals.

1 Ion size parameters for common ions may be found in many references. (Strumm and Morgan, 1970; Kielland, 1937; Klotz, 1950; Garrels and Christ, 1965; Butler, 1964).

2 Determined from values contained in Chemical Rubber Company (1964).

3 Equivalent Conductivity is in cm<sup>2</sup>mho per equivalent and the values are taken from Robinson and Stokes (1970). Comparable values are also listed by Harned and Owen (1958).

Table A7-3. Expansive coefficients  $C_n$  used in the full conductivity equation.

$$C_0 = 1/2(2 - \sqrt{2}) \qquad C_n = \frac{\sqrt{2}}{2} \binom{1/2}{n} \text{ for } n \geq 1$$

$$C_0 = 0.2929 \qquad C_3 = -0.0442$$

$$C_1 = -0.3536 \qquad C_4 = 0.0276$$

$$C_2 = 0.0884 \qquad C_5 = -0.0193$$

(Onsager and Fuoss, 1932)

Table A7-4. Dissociation constants.

Ligand	Ion Complex	log $\kappa$	Source	Temp °C	Remarks	
$\text{SO}_4^{=}$	$\text{HSO}_4^-$	1.92	5	25	Important at pH < 3.3*	
		2.	6	25		
	$\text{NaSO}_4^-$	0.72	1,6	25	Important for $\{\text{SO}_4^{=}\} > 10^{-2.0}$	
		0.65	3	25		
		0.70	4	18		
	$\text{KSO}_4^-$	0.96	1,6	25	Important for $\{\text{SO}_4^{=}\} > 10^{-2.3}$	
		0.75	3	25		
		0.82	4	18		
	$\text{CaSO}_4^0$	2.31	1,2,3,6	25	Important for $\{\text{SO}_4^{=}\} > 10^{-3.6}$	
		2.27	2	25		
		2.57	2	25		
		2.43	3	25		
		2.27	4	18		
	$\text{MgSO}_4^0$	2.21	1	25	Important for $\{\text{SO}_4^{=}\} > 10^{-3.7}$	
		2.27	1	25		
		2.20	1,4	25		
		2.36	1,6	25		
		2.23	3	25		
		2.40	3	25		
		2.34	3	25		
2.22		2	25			
2.25		2	25			
$\text{HCO}_3^-$		$\text{H}_2\text{CO}_3^0$	6.4	6.		25
	- 0.25		1,6	25		
	$\text{NaHCO}_3^0$	1.26	1,6	25	Important for $\{\text{HCO}_3^-\} > 10^{-2.6}$	
	$\text{CaHCO}_3^+$	1.16	1,6	25	Important for $\{\text{HCO}_3^-\} > 10^{-2.5}$	
	$\text{MgHCO}_3^+$	3.7	1	25		
		0.95	2	25		
		0.86	2	25		
		0.77	1	22		
	$\text{CO}_3^{=}$	$\text{HCO}_3^-$	10.33	6	25	
		$\text{NaCO}_3$	1.27	1,6	25	
$\text{CaCO}_3$		3.2	1,6	25		
$\text{MgCO}_3$		3.4	1,6	25		
$\text{OH}^-$	$\text{H}_2\text{O}^0$	14.0	6	25	Important for pH > 13.3	
		- 0.57	1	25		
	$\text{NaOH}$	- 0.77	1	25		
		- 0.70	1,6	25		
		$\text{CaOH}^+$	1.51	1	25	Important for pH > 11.4
		1.29	1	25		
		1.30	1,6	25		
		1.51	4	25		
		1.40	5	30		
	$\text{MgOH}^+$	2.58	1,6	25	Important for pH > 10.1	
	2.60	2	25			
$\text{NO}_3^-$	$\text{NaNO}_3^-$	- 0.3	1	25	Nitrate complexes are rarely, if ever, of importance	
		to -0.5	1	25		
	$\text{KNO}_3^-$	- 0.24	1	25		
		- 0.15	1	25		
		- 0.15	4	18		
	$\text{CaNO}_3^+$	0.28	4	18		

## Sources:

1. Sillen and Martell, 1964
2. Sillen and Martell, 1971
3. Christenson and Izatt, 1970
4. Harmed and Owen, 1958
5. CRC Tables, 1964
6. Garrels and Christ, 1965

\* Limits given are generally where approximately 5 percent of the cations (Ligand in the case of  $\text{HSO}_4^-$ ) are complexed.



Table A7-5. Results from application of conductivity formulas.

<u>Measured Conductivity</u>	<u>Calculated Conductivity</u>		<u>Remarks</u>	
	<u>Full Equation</u>	<u>Simplified Equation</u>		
130.	130.	130.	Single Salt Solutions: Data from Table A7-1	
10240.	10146.	10034.		
561.	564.	564.		
1145.	1151.	1145.		
123.	123.	123.		
10674.	10634.	10631.		
585.	588.	585.		
2650.	2615.	2612.		<u>Saline River</u>
2170.	2248.	2247.		
1100.	1104.	1103.		
4870.	4811.	4806.		
1730.	1700.	1699.		
347.	352.	352.	<u>Wind River</u>	
265.	266.	265.		
730.	747.	748.		
367.	372.	372.		
422.	403.	403.		
1410.	1337.	1338.	<u>Pecos River</u>	
865.	860.	860.		
2720.	2722.	2722.		
2500.	2531.	2532.		
570.	568.	569.		
1530.	1508.	1510.	<u>Henry's Fork River</u>	
973.	978.	979.		
1040.	1056.	1057.		
2200.	2215.	2214.		
1180.	1202.	1203.		
246.	238.	237.	<u>New Fork River</u>	
204.	206.	205.		
220.	210.	210.		
116.	111.	110.		
60.	59.	59.		
577.	543.	549.	<u>Kiskiminetas River at Leechburg, Pa. (pH &lt; 4.0)</u>	
1410.	1310.	1333.		
466.	465.	472.		

Table A7-6. Sample conductivity calculation.

Date of Composite Sample: 10/1/59 - 10/31/59  
 Location: Henry's Fork River  
 Measured Conductivity: 1600  $\mu\text{U}/\text{cm}$   
 Measured Flow: 33.3 cfs  
 Total Dissolved Solids: 1220 ppm  
 Sodium Absorption Ratio: 1.3  
 pH: 8.1

	<u>Measured Concentration</u>		<u>Equilibrium</u>	<u>Equivalent</u>
	<u>ppm</u>	<u>meq/l</u>	<u>Species</u> <u>meq/l</u>	<u>Conductance</u> <u><math>\lambda</math></u>
Fe <sup>++</sup>	0.01	0.000	0.000	77.38
Ca <sup>++</sup>	158	7.884	5.905	45.81
Mg <sup>++</sup>	96	7.897	5.826	40.82
Na <sup>++</sup>	83	3.610	3.554	44.11
K <sup>+</sup>	11	0.281	0.275	65.84
H <sup>+</sup>	--	0.000	0.000	322.54
Mn <sup>++</sup>	--	-----	0.000	31.09
CaHCO <sub>3</sub> <sup>+</sup>	--	-----	0.119	62.58
MgHCO <sub>3</sub> <sup>+</sup>	--	-----	0.093	62.58
CaOH <sup>+</sup>	--	-----	0.000	62.58
MgOH <sup>+</sup>	--	-----	<u>0.000</u>	62.58
		$\Sigma = 19.672$	$\Sigma = 15.772$	
OH <sup>-</sup>	--	0.001	0.001	182.00
Cl <sup>-</sup>	36	1.015	1.015	69.29
F <sup>-</sup>	--	-----	0.000	49.63
NO <sub>3</sub> <sup>-</sup>	0.9	0.015	0.015	64.70
NaSO <sub>4</sub> <sup>-</sup>	--	-----	0.050	63.32
KSO <sub>4</sub> <sup>-</sup>	--	-----	0.007	63.32
HSO <sub>4</sub> <sup>-</sup>	--	-----	0.000	63.51
NaCO <sub>3</sub> <sup>-</sup>	--	-----	0.000	63.32
HCO <sub>3</sub> <sup>-</sup>	237	4.474	4.257	39.34
CO <sub>3</sub> <sup>=</sup>	--	-----	0.007	54.98
SO <sub>4</sub> <sup>-</sup>	676	<u>14.074</u>	<u>10.422</u>	63.46
		$\Sigma = 19.579$	$\Sigma = 15.774$	
		<u>moles/l</u>	<u>moles/l</u>	
B	0.28	0.026	0.026	
SiO <sub>2</sub>	21	0.350	0.350	
CaSO <sub>4</sub>	--	-----	0.841	
MgSO <sub>4</sub>	--	-----	0.929	
CaCO <sub>3</sub>	--	-----	0.030	
MgCO <sub>3</sub>	--	-----	0.014	
NaHCO <sub>3</sub>	--	-----	0.006	
NaOH	--	-----	0.000	

Calculated Conductance (Full Equation) = 1601.2  $\mu\text{U}/\text{cm}$

Table A9-1. Chemical analyses predicted from flow records for the Henry's Fork River for the water year beginning October 1, 1970 (concentrations in parts per million).

Measured Mean daily discharge	Conductivity μJ/cm	Ca	Mg	Na	K	Fe	pH	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	F	NO <sub>3</sub>	B	SiO <sub>2</sub>	Day of Year
42.	1403.	7.9	5.9	2.7	.27	.0030	7.9	5.2	10.8	.74	.037	.019	.023	.43	1
43.	1401.	7.9	5.9	2.7	.27	.0031	7.9	5.2	10.8	.74	.037	.019	.023	.43	2
43.	1404.	7.9	5.9	2.7	.27	.0031	7.9	5.2	10.8	.74	.037	.019	.023	.43	3
43.	1406.	7.9	5.9	2.7	.27	.0031	7.9	5.2	10.8	.74	.037	.019	.023	.43	4
43.	1409.	7.9	5.9	2.8	.28	.0031	7.9	5.2	10.8	.75	.037	.019	.023	.43	5
46.	1397.	7.9	5.8	2.7	.27	.0031	7.9	5.2	10.7	.74	.037	.019	.023	.43	6
56.	1356.	7.7	5.6	2.6	.27	.0032	7.9	5.2	10.2	.71	.037	.018	.022	.43	7
62.	1336.	7.6	5.5	2.5	.27	.0033	7.9	5.2	9.9	.69	.038	.018	.022	.43	8
68.	1318.	7.5	5.4	2.5	.27	.0033	7.9	5.2	9.7	.68	.038	.018	.022	.42	9
75.	1299.	7.4	5.3	2.4	.28	.0034	7.9	5.2	9.5	.66	.038	.018	.021	.42	10
82.	1280.	7.3	5.2	2.4	.26	.0034	7.9	5.2	9.2	.65	.038	.017	.021	.42	11
75.	1300.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.5	.66	.038	.018	.021	.42	12
78.	1292.	7.3	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	13
79.	1290.	7.3	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	14
77.	1296.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	15
75.	1301.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.5	.66	.038	.018	.021	.42	16
77.	1296.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	17
76.	1298.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	18
76.	1298.	7.4	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	19
78.	1292.	7.3	5.3	2.4	.26	.0034	7.9	5.2	9.4	.66	.038	.017	.021	.42	20
74.	1304.	7.4	5.4	2.4	.26	.0034	7.9	5.2	9.5	.67	.038	.018	.021	.42	21
82.	1278.	7.3	5.2	2.4	.26	.0034	7.9	5.2	9.2	.65	.038	.017	.021	.42	22
87.	1264.	7.2	5.1	2.3	.26	.0034	7.9	5.2	9.1	.64	.038	.017	.021	.42	23
84.	1271.	7.2	5.2	2.4	.26	.0034	7.9	5.2	9.2	.64	.038	.017	.021	.42	24
86.	1265.	7.2	5.2	2.5	.26	.0034	7.9	5.2	9.1	.64	.038	.017	.021	.42	25
70.	1313.	7.4	5.4	2.5	.27	.0033	7.9	5.2	9.6	.67	.038	.018	.021	.42	26
64.	1334.	7.5	5.5	2.5	.27	.0033	7.9	5.2	9.9	.69	.038	.018	.022	.43	27
62.	1341.	7.6	5.5	2.5	.27	.0033	7.9	5.2	10.0	.69	.038	.018	.022	.43	28
70.	1310.	7.4	5.4	2.5	.26	.0033	7.9	5.2	9.6	.67	.038	.018	.021	.42	29
80.	1275.	7.2	5.2	2.4	.26	.0034	7.9	5.1	9.2	.65	.037	.017	.021	.42	30
86.	1257.	7.1	5.1	2.3	.26	.0034	7.9	5.1	9.0	.63	.037	.017	.020	.42	31
87.	1252.	7.1	5.1	2.3	.26	.0034	7.9	5.1	9.0	.63	.037	.017	.020	.41	32
82.	1265.	7.2	5.2	2.3	.26	.0033	7.9	5.1	9.1	.64	.037	.017	.021	.42	33
74.	1290.	7.3	5.3	2.4	.26	.0033	7.9	5.1	9.4	.66	.037	.017	.021	.42	34
67.	1313.	7.4	5.4	2.5	.26	.0033	7.9	5.2	9.7	.67	.037	.018	.021	.42	35
81.	1263.	7.2	5.2	2.3	.26	.0033	7.9	5.1	9.1	.64	.037	.017	.021	.41	36
90.	1235.	7.0	5.0	2.3	.25	.0034	7.9	5.1	8.8	.62	.037	.017	.020	.41	37
95.	1220.	6.9	4.9	2.2	.25	.0034	7.9	5.0	8.6	.61	.037	.016	.020	.41	38
94.	1221.	6.9	4.9	2.2	.25	.0034	7.9	5.0	8.7	.61	.037	.016	.020	.41	39
85.	1244.	7.0	5.1	2.3	.25	.0033	7.9	5.0	8.9	.63	.037	.017	.020	.41	40
95.	1214.	6.9	4.9	2.2	.25	.0033	7.9	5.0	8.6	.61	.037	.016	.020	.40	41
70.	1290.	7.3	5.3	2.4	.26	.0033	7.9	5.1	9.4	.66	.037	.017	.021	.42	42
73.	1277.	7.2	5.2	2.4	.26	.0033	7.9	5.1	9.3	.65	.037	.017	.021	.41	43
78.	1258.	7.1	5.1	2.3	.26	.0033	7.9	5.0	9.1	.64	.037	.017	.020	.41	44
47.	1395.	7.8	5.8	2.7	.27	.0031	7.9	5.2	10.6	.73	.037	.019	.023	.43	45
48.	1387.	7.8	5.8	2.7	.27	.0031	7.9	5.2	10.6	.73	.037	.019	.023	.43	46
74.	1266.	7.2	5.2	2.4	.26	.0032	7.9	5.0	9.2	.64	.037	.017	.021	.41	47
72.	1272.	7.2	5.2	2.4	.26	.0032	7.9	5.0	9.3	.65	.037	.017	.021	.41	48
65.	1298.	7.3	5.3	2.4	.26	.0032	7.9	5.1	9.6	.67	.037	.018	.021	.41	49
69.	1279.	7.2	5.2	2.4	.26	.0032	7.9	5.0	9.4	.65	.037	.017	.021	.41	50
67.	1237.	7.3	5.3	2.4	.26	.0032	7.9	5.1	9.4	.66	.037	.017	.021	.41	51
85.	1222.	6.9	5.0	2.2	.25	.0033	7.9	4.9	8.7	.61	.036	.016	.020	.40	52
91.	1202.	6.7	4.8	2.2	.24	.0032	7.9	4.8	8.4	.59	.035	.016	.019	.39	53
85.	1219.	6.9	4.9	2.2	.25	.0032	7.9	4.9	8.7	.61	.036	.016	.020	.40	54
95.	1189.	6.6	4.7	2.1	.24	.0032	7.9	4.8	8.3	.58	.035	.016	.019	.39	55
127.	1116.	6.3	4.4	2.0	.23	.0033	7.9	4.7	7.6	.54	.035	.015	.018	.38	56
112.	1146.	6.4	4.5	2.0	.23	.0033	7.9	4.7	7.8	.56	.035	.015	.018	.38	57
86.	1210.	6.7	4.8	2.2	.24	.0032	7.9	4.8	8.5	.60	.035	.016	.019	.39	58
63.	1291.	7.3	5.3	2.4	.26	.0031	7.9	5.0	9.5	.66	.036	.017	.021	.41	59
65.	1281.	7.2	5.3	2.4	.26	.0032	7.9	5.0	9.4	.66	.036	.017	.021	.41	60
67.	1271.	7.2	5.2	2.4	.25	.0032	7.9	5.0	9.3	.65	.036	.017	.021	.41	61
72.	1251.	7.0	5.1	2.3	.25	.0032	7.9	5.0	9.1	.64	.036	.017	.020	.40	62
74.	1243.	7.0	5.1	2.3	.25	.0032	7.9	4.9	9.0	.63	.036	.017	.020	.40	63
72.	1249.	7.0	5.1	2.3	.25	.0032	7.9	4.9	9.1	.64	.036	.017	.020	.40	64
68.	1263.	7.1	5.2	2.4	.25	.0031	7.9	5.0	9.2	.65	.036	.017	.021	.40	65
70.	1254.	7.1	5.1	2.3	.25	.0032	7.9	4.9	9.1	.64	.036	.017	.020	.40	66
76.	1232.	6.9	5.0	2.3	.25	.0032	7.9	4.9	8.9	.62	.036	.016	.020	.40	67
80.	1218.	6.9	4.9	2.2	.25	.0032	7.9	4.9	8.7	.61	.036	.016	.020	.40	68
83.	1207.	6.7	4.8	2.2	.24	.0031	7.9	4.8	8.5	.60	.035	.016	.019	.39	69
83.	1206.	6.7	4.8	2.2	.24	.0031	7.9	4.8	8.5	.59	.035	.016	.019	.39	70
80.	1216.	6.8	4.9	2.2	.25	.0032	7.9	4.9	8.7	.61	.035	.016	.020	.40	71
80.	1215.	6.8	4.9	2.2	.25	.0032	7.9	4.9	8.7	.61	.035	.016	.020	.40	72
77.	1224.	6.9	5.0	2.3	.25	.0032	7.9	4.9	8.8	.62	.035	.016	.020	.40	73
74.	1233.	6.9	5.0	2.3	.25	.0031	7.9	4.9	8.9	.63	.036	.017	.020	.40	74
67.	1258.	7.1	5.1	2.4	.25	.0031	7.9	4.9	9.2	.64	.036	.017	.020	.40	75
63.	1273.	7.2	5.2	2.4	.25	.0031	7.9	4.9	9.4	.65	.036	.017	.021	.40	76
55.	1309.	7.3	5.4	2.5	.26	.0031	7.9	5.0	9.8	.68	.036	.018	.021	.41	77
56.	1303.	7.3	5.4	2.5	.26	.0031	7.9	5.0	9.7	.67	.036	.018	.021	.41	78
57.	1297.	7.3	5.3	2.5	.26	.0031	7.9	5.0	9.6	.67	.036	.018	.021	.41	79
54.	1310.	7.3	5.4	2.5	.26	.0030	7.9	5.0	9.8	.68	.036	.018	.021	.41	80

Measured Mean Daily Discharge	Conduc- tivity µS/cm	Ca	Mg	Na	K	Fe	pH	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	F	NO <sub>3</sub>	B	SiO <sub>2</sub>	Day of Year
50.	1330.	7.5	5.5	2.6	.26	.0030	7.9	5.0	10.0	.69	.036	.018	.022	.41	81
48.	1339.	7.5	5.6	2.6	.26	.0030	7.9	5.0	10.1	.70	.036	.018	.022	.41	82
47.	1343.	7.5	5.6	2.6	.26	.0030	7.9	5.0	10.2	.70	.036	.018	.022	.41	83
48.	1336.	7.5	5.6	2.6	.26	.0030	7.9	5.0	10.1	.70	.036	.018	.022	.41	84
50.	1324.	7.4	5.5	2.5	.26	.0030	7.9	5.0	10.0	.69	.036	.018	.022	.41	85
53.	1308.	7.3	5.4	2.5	.26	.0030	7.9	5.0	9.8	.68	.036	.018	.021	.41	86
53.	1304.	7.3	5.4	2.5	.26	.0030	7.9	4.9	9.8	.68	.035	.018	.021	.40	89
54.	1298.	7.3	5.4	2.5	.26	.0030	7.9	4.9	9.7	.67	.035	.018	.021	.40	90
55.	1292.	7.2	5.3	2.5	.25	.0030	7.9	4.9	9.6	.67	.035	.017	.021	.40	91
56.	1285.	7.2	5.3	2.4	.25	.0030	7.9	4.9	9.6	.66	.035	.017	.021	.40	92
51.	1307.	7.3	5.4	2.5	.26	.0030	7.9	4.9	9.8	.68	.035	.018	.021	.40	93
48.	1320.	7.4	5.5	2.5	.26	.0030	7.9	4.9	10.0	.69	.035	.018	.022	.40	94
43.	1345.	7.5	5.6	2.6	.26	.0029	7.9	5.0	10.3	.71	.035	.018	.022	.41	95
38.	1375.	7.7	5.8	2.7	.26	.0029	7.9	5.0	10.6	.73	.035	.019	.023	.41	96
35.	1394.	7.8	5.9	2.8	.27	.0028	7.9	5.0	10.8	.74	.035	.019	.023	.41	97
32.	1414.	7.9	6.0	2.8	.27	.0028	7.9	5.0	11.1	.76	.035	.019	.023	.41	98
30.	1428.	7.9	6.1	2.9	.27	.0028	7.9	5.0	11.3	.77	.035	.020	.024	.41	99
32.	1408.	7.8	5.9	2.8	.27	.0028	7.9	5.0	11.0	.75	.035	.019	.023	.41	100
33.	1397.	7.8	5.9	2.8	.27	.0028	7.9	5.0	10.9	.75	.035	.019	.023	.41	101
33.	1394.	7.7	5.9	2.8	.27	.0028	7.9	4.9	10.9	.75	.035	.019	.023	.41	102
34.	1383.	7.7	5.8	2.7	.26	.0028	7.9	4.9	10.8	.74	.035	.019	.023	.41	103
35.	1373.	7.6	5.8	2.7	.26	.0028	7.9	4.9	10.7	.73	.034	.019	.022	.40	104
40.	1337.	7.4	5.6	2.6	.26	.0028	7.9	4.9	10.3	.71	.034	.018	.022	.40	105
45.	1307.	7.3	5.4	2.5	.25	.0029	7.9	4.8	9.9	.68	.034	.018	.021	.40	106
50.	1279.	7.1	5.3	2.4	.25	.0029	7.9	4.8	9.6	.66	.034	.017	.021	.39	107
80.	1175.	6.5	4.7	2.1	.23	.0030	7.9	4.6	8.3	.58	.034	.015	.019	.37	108
120.	1093.	6.1	4.3	1.9	.22	.0032	7.9	4.6	7.4	.53	.034	.014	.017	.37	109
190.	1008.	6.7	3.9	1.7	.22	.0034	7.9	4.5	6.6	.47	.034	.013	.016	.36	110
300.	930.	5.4	3.6	1.5	.21	.0036	7.9	4.4	5.8	.43	.034	.012	.015	.36	111
270.	946.	5.4	3.6	1.6	.21	.0036	7.9	4.4	6.0	.44	.034	.012	.015	.36	112
200.	996.	5.7	3.4	1.7	.21	.0034	7.9	4.5	6.5	.47	.034	.013	.016	.36	113
150.	1044.	5.8	4.1	1.8	.22	.0033	7.9	4.5	7.0	.50	.034	.014	.017	.36	114
130.	1068.	6.0	4.2	1.9	.22	.0032	7.9	4.5	7.2	.51	.034	.014	.017	.36	115
130.	1067.	6.0	4.2	1.9	.22	.0032	7.9	4.5	7.2	.51	.034	.014	.017	.36	116
120.	1079.	6.0	4.2	1.9	.22	.0031	7.9	4.5	7.3	.52	.033	.014	.017	.36	117
130.	1063.	6.0	4.2	1.9	.22	.0032	7.9	4.5	7.2	.51	.033	.014	.017	.36	118
130.	1061.	6.0	4.2	1.9	.22	.0032	7.9	4.5	7.2	.51	.033	.014	.017	.36	119
125.	1066.	6.0	4.2	1.9	.22	.0031	7.9	4.5	7.2	.51	.033	.014	.017	.36	120
115.	1079.	6.0	4.3	1.9	.22	.0031	7.9	4.5	7.4	.52	.033	.014	.017	.36	121
100.	1101.	6.1	4.4	2.0	.22	.0030	7.9	4.5	7.6	.54	.033	.014	.017	.36	122
86.	1127.	6.2	4.5	2.0	.23	.0030	7.9	4.5	7.9	.55	.033	.015	.018	.36	123
76.	1148.	6.3	4.6	2.1	.23	.0029	7.9	4.5	8.1	.57	.033	.015	.018	.36	124
65.	1175.	6.4	4.7	2.2	.23	.0028	7.9	4.5	8.4	.59	.032	.015	.019	.36	125
58.	1194.	6.5	4.8	2.2	.23	.0028	7.9	4.5	8.6	.60	.032	.016	.019	.36	126
55.	1202.	6.5	4.8	2.2	.23	.0027	7.9	4.5	8.7	.61	.032	.016	.019	.36	127
51.	1215.	6.6	4.9	2.3	.23	.0027	7.9	4.4	8.9	.61	.032	.016	.019	.36	128
60.	1180.	6.4	4.7	2.2	.23	.0028	7.9	4.4	8.5	.59	.032	.015	.019	.36	129
70.	1149.	6.3	4.6	2.1	.23	.0028	7.9	4.4	8.2	.57	.032	.015	.018	.36	130
80.	1122.	6.2	4.5	2.0	.22	.0029	7.9	4.4	7.9	.55	.032	.015	.018	.36	131
80.	1119.	6.2	4.4	2.0	.22	.0029	7.9	4.4	7.9	.55	.032	.015	.018	.36	132
84.	1109.	6.1	4.4	2.0	.22	.0029	7.9	4.4	7.8	.55	.032	.015	.018	.36	133
90.	1094.	6.1	4.3	2.0	.22	.0029	7.9	4.4	7.6	.54	.032	.014	.017	.35	134
94.	1085.	6.0	4.3	1.9	.22	.0029	7.9	4.4	7.5	.53	.032	.014	.017	.35	135
94.	1083.	6.0	4.3	1.9	.22	.0029	7.9	4.4	7.5	.53	.032	.014	.017	.35	136
90.	1089.	6.0	4.3	2.0	.22	.0029	7.9	4.4	7.6	.53	.032	.014	.017	.35	137
84.	1099.	6.1	4.4	2.0	.22	.0029	7.9	4.3	7.7	.54	.032	.014	.017	.35	138
76.	1115.	6.1	4.4	2.0	.22	.0028	7.9	4.3	7.9	.55	.032	.015	.018	.35	139
66.	1140.	6.2	4.6	2.1	.22	.0027	7.9	4.3	8.1	.57	.031	.015	.018	.35	140
60.	1156.	6.3	4.6	2.1	.22	.0027	8.0	4.3	8.3	.58	.031	.015	.018	.35	141
57.	1164.	6.3	4.7	2.1	.22	.0027	8.0	4.3	8.4	.58	.031	.015	.018	.35	142
50.	1188.	6.4	4.8	2.2	.23	.0026	8.0	4.3	8.7	.60	.031	.016	.019	.35	143
43.	1218.	6.6	4.9	2.3	.23	.0026	8.0	4.3	9.0	.62	.031	.016	.019	.36	144
37.	1247.	6.8	5.2	2.4	.24	.0025	8.0	4.4	9.5	.65	.031	.017	.020	.36	145
37.	1246.	6.8	5.2	2.4	.24	.0025	8.0	4.4	9.5	.65	.031	.017	.020	.36	146
39.	1235.	6.6	5.0	2.3	.23	.0025	8.0	4.3	9.2	.63	.031	.016	.020	.36	147
43.	1214.	6.6	4.9	2.3	.23	.0025	8.0	4.3	9.0	.62	.031	.016	.019	.35	148
44.	1209.	6.5	4.9	2.3	.23	.0026	8.0	4.3	8.9	.61	.031	.016	.019	.35	149
40.	1228.	6.6	5.0	2.3	.23	.0025	8.0	4.3	9.1	.63	.031	.016	.019	.36	150
37.	1244.	6.8	5.1	2.4	.24	.0025	8.0	4.4	9.5	.65	.031	.017	.020	.36	151
35.	1256.	6.9	5.2	2.4	.24	.0025	8.0	4.4	9.6	.66	.031	.017	.020	.36	152
35.	1256.	6.9	5.2	2.4	.24	.0025	8.0	4.4	9.6	.66	.031	.017	.020	.36	153
38.	1238.	6.8	5.1	2.4	.23	.0025	8.0	4.4	9.4	.65	.031	.017	.020	.36	154
38.	1238.	6.8	5.1	2.4	.23	.0025	8.0	4.4	9.4	.65	.031	.017	.020	.36	155
35.	1256.	6.9	5.2	2.4	.24	.0025	8.0	4.4	9.6	.66	.031	.017	.020	.36	156
33.	1270.	7.0	5.3	2.5	.24	.0025	8.0	4.4	9.8	.67	.031	.017	.021	.37	157
35.	1257.	6.9	5.2	2.4	.24	.0025	8.0	4.4	9.6	.66	.031	.017	.020	.37	158
40.	1229.	6.6	5.0	2.3	.23	.0025	8.0	4.3	9.1	.63	.031	.016	.019	.36	159
45.	1202.	6.5	4.8	2.3	.23	.0025	8.0	4.3	8.9	.61	.031	.016	.019	.35	160
50.	1180.	6.4	4.7	2.2	.22	.0026	8.0	4.3	8.6	.60	.031	.015	.019	.35	161
58.	1149.	6.3	4.6	2.1	.22	.0027	8.0	4.3	8.3	.58	.031	.015	.018	.35	162
67.	1118.	6.1	4.5	2.0	.22	.0027	8.0	4.3	8.0	.56	.031	.015	.018	.35	163
69.	1112.	6.1	4.4	2.0	.22	.0027	8.0	4.3	7.9	.55	.031	.015	.018	.35	164
66.	1121.	6.1	4.5	2.0	.22	.0027	8.0	4.3	8.0	.56	.031	.015	.018	.35	165
70.	1108.	6.1	4.4	2.0	.22	.0027	8.0	4.3	7.9	.55	.031	.015	.018	.35	166
76.	1091.	6.0	4.3	2.0	.22	.0027	8.0	4.2	7.7	.54	.031	.014	.017	.35	167

Measured Mean Daily Discharge	Conduc- tivity µS/cm	Ca	Mg	Na	K	Fe	pH	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	F	NO <sub>3</sub>	B	SiO <sub>2</sub>	Day of Year
70.	1107.	6.1	4.4	2.0	.22	.0027	8.0	4.3	7.9	.55	.031	.015	.018	.35	168
67.	1116.	6.1	4.5	2.0	.22	.0027	8.0	4.3	8.0	.56	.031	.015	.018	.35	169
74.	1094.	6.0	4.4	2.0	.22	.0027	8.0	4.2	7.7	.54	.031	.014	.017	.35	170
80.	1077.	5.9	4.3	1.9	.21	.0028	8.0	4.2	7.6	.53	.031	.014	.017	.34	171
100.	1028.	5.7	4.1	1.8	.21	.0028	8.0	4.2	7.1	.50	.031	.013	.016	.34	173
150.	946.	5.3	3.7	1.6	.20	.0030	7.9	4.1	6.3	.45	.031	.012	.015	.33	174
210.	881.	5.0	3.4	1.5	.19	.0031	7.9	4.0	5.7	.41	.030	.011	.014	.32	175
330.	800.	4.5	3.0	1.3	.17	.0031	7.9	3.7	4.8	.35	.029	.010	.012	.30	176
417.	760.	4.3	2.8	1.2	.17	.0032	8.0	3.7	4.4	.33	.029	.009	.012	.29	177
575.	707.	4.0	2.6	1.1	.16	.0032	8.0	3.5	3.9	.30	.028	.009	.011	.28	178
369.	773.	4.3	2.9	1.2	.17	.0031	8.0	3.7	4.6	.34	.029	.010	.012	.30	179
338.	784.	4.4	2.9	1.3	.17	.0031	8.0	3.7	4.7	.34	.029	.010	.012	.30	180
254.	831.	4.6	3.1	1.4	.18	.0030	8.0	3.8	5.1	.36	.029	.010	.013	.30	181
120.	973.	5.4	3.8	1.7	.20	.0028	8.0	4.1	6.6	.47	.030	.013	.015	.33	182
73.	1083.	6.0	4.3	2.0	.21	.0027	8.0	4.2	7.7	.54	.030	.014	.017	.34	183
62.	1121.	6.1	4.5	2.1	.22	.0026	8.0	4.2	8.1	.56	.031	.015	.018	.35	184
67.	1100.	6.0	4.4	2.0	.21	.0027	8.0	4.2	7.9	.55	.030	.014	.017	.34	185
67.	1098.	6.0	4.4	2.0	.21	.0027	8.0	4.2	7.8	.55	.030	.014	.017	.34	186
66.	1100.	6.0	4.4	2.0	.21	.0026	8.0	4.2	7.9	.55	.030	.014	.017	.34	187
76.	1063.	5.9	4.2	1.9	.21	.0027	8.0	4.1	7.5	.53	.030	.014	.017	.34	188
82.	1042.	5.8	4.1	1.9	.21	.0027	8.0	4.1	7.3	.51	.030	.014	.016	.33	189
73.	1068.	5.9	4.3	1.9	.21	.0027	8.0	4.1	7.6	.53	.030	.014	.017	.34	190
79.	1045.	5.8	4.2	1.9	.21	.0027	8.0	4.1	7.4	.52	.030	.014	.017	.33	191
79.	1042.	5.7	4.1	1.9	.21	.0027	8.0	4.1	7.3	.52	.030	.014	.016	.33	192
80.	1036.	5.7	4.1	1.9	.21	.0027	8.0	4.1	7.3	.51	.030	.014	.016	.33	193
88.	1010.	5.6	4.0	1.8	.20	.0027	8.0	4.0	7.1	.50	.029	.013	.016	.33	194
84.	1018.	5.6	4.0	1.8	.20	.0026	8.0	4.0	7.1	.50	.029	.013	.016	.33	195
87.	1006.	5.6	4.0	1.8	.20	.0026	8.0	4.0	7.0	.49	.029	.013	.016	.32	196
87.	1003.	5.5	4.0	1.8	.20	.0026	8.0	4.0	7.0	.49	.029	.013	.016	.32	197
88.	997.	5.5	4.0	1.8	.20	.0026	8.0	4.0	7.0	.49	.029	.013	.016	.32	198
90.	988.	5.5	3.9	1.8	.20	.0025	8.0	3.9	6.9	.48	.029	.013	.016	.32	199
90.	984.	5.4	3.9	1.8	.20	.0026	8.0	3.9	6.9	.48	.029	.013	.016	.32	200
120.	912.	5.1	3.6	1.6	.19	.0027	8.0	3.8	6.2	.44	.028	.012	.014	.31	201
130.	889.	4.9	3.4	1.5	.18	.0026	8.0	3.7	5.9	.42	.027	.011	.014	.30	202
126.	892.	4.9	3.4	1.5	.18	.0026	8.0	3.7	5.9	.42	.027	.011	.014	.30	203
202.	787.	4.3	3.0	1.3	.16	.0026	8.0	3.4	4.9	.36	.026	.010	.012	.28	204
254.	738.	4.1	2.7	1.2	.16	.0026	8.0	3.3	4.5	.33	.025	.009	.011	.27	205
198.	783.	4.3	2.9	1.3	.16	.0026	8.0	3.4	4.9	.36	.026	.010	.012	.27	206
192.	785.	4.3	2.9	1.3	.16	.0026	8.0	3.4	4.9	.36	.026	.010	.012	.27	207
160.	819.	4.5	3.1	1.4	.17	.0025	8.0	3.5	5.3	.38	.026	.010	.013	.28	208
144.	838.	4.6	3.2	1.4	.17	.0025	8.0	3.5	5.4	.39	.026	.011	.013	.28	209
134.	850.	4.6	3.2	1.4	.17	.0025	8.0	3.5	5.6	.40	.026	.011	.013	.28	210
132.	849.	4.6	3.2	1.4	.17	.0025	8.0	3.5	5.6	.40	.026	.011	.013	.28	211
130.	848.	4.6	3.2	1.4	.17	.0025	8.0	3.5	5.6	.40	.026	.011	.013	.28	212
110.	883.	4.8	3.4	1.5	.18	.0024	8.0	3.6	5.9	.42	.026	.011	.014	.29	213
120.	859.	4.7	3.3	1.5	.17	.0024	8.0	3.5	5.7	.40	.026	.011	.013	.28	214
132.	833.	4.5	3.2	1.4	.17	.0024	8.0	3.4	5.5	.39	.026	.011	.013	.28	215
144.	810.	4.4	3.1	1.4	.16	.0024	8.0	3.4	5.2	.38	.025	.010	.012	.27	216
154.	792.	4.3	3.0	1.3	.16	.0024	8.0	3.3	5.1	.36	.025	.010	.012	.27	217
151.	792.	4.3	3.0	1.3	.16	.0024	8.0	3.3	5.1	.36	.025	.010	.012	.27	218
156.	782.	4.3	2.9	1.3	.16	.0024	8.0	3.3	5.0	.36	.025	.010	.012	.26	219
180.	749.	4.1	2.8	1.2	.15	.0024	8.0	3.2	4.7	.34	.024	.009	.011	.26	220
156.	776.	4.2	2.9	1.3	.16	.0024	8.0	3.2	5.0	.36	.024	.010	.012	.26	221
165.	761.	4.1	2.9	1.3	.15	.0024	8.0	3.2	4.8	.35	.024	.009	.012	.26	222
144.	787.	4.3	3.0	1.3	.16	.0023	8.0	3.3	5.1	.36	.024	.010	.012	.26	223
136.	696.	4.3	3.0	1.3	.16	.0023	8.0	3.3	5.2	.37	.024	.010	.012	.26	224
151.	771.	4.2	2.9	1.3	.16	.0023	8.0	3.2	4.9	.35	.024	.010	.012	.26	225
165.	750.	4.1	2.8	1.2	.15	.0023	8.1	3.1	4.7	.34	.024	.009	.011	.25	226
168.	744.	4.0	2.8	1.2	.15	.0023	8.1	3.1	4.7	.34	.024	.009	.011	.25	227
188.	719.	3.9	2.7	1.2	.15	.0023	8.1	3.1	4.5	.32	.023	.009	.011	.25	228
212.	693.	3.8	2.6	1.1	.14	.0023	8.1	3.0	4.2	.31	.023	.008	.010	.24	229
185.	718.	3.9	2.7	1.2	.15	.0023	8.1	3.0	4.5	.32	.023	.009	.011	.25	230
165.	739.	4.0	2.8	1.2	.15	.0023	8.1	3.1	4.7	.34	.023	.009	.011	.25	231
147.	763.	4.1	2.9	1.3	.15	.0023	8.1	3.2	4.9	.35	.024	.010	.012	.25	232
142.	768.	4.2	2.9	1.3	.15	.0023	8.1	3.2	4.9	.35	.024	.010	.012	.26	233
128.	789.	4.3	3.0	1.3	.16	.0023	8.1	3.2	5.1	.37	.024	.010	.012	.26	234
144.	763.	4.1	2.9	1.3	.15	.0023	8.1	3.1	4.9	.35	.024	.010	.012	.25	235
170.	728.	3.9	2.7	1.2	.15	.0023	8.1	3.1	4.6	.33	.023	.009	.011	.25	236
160.	739.	4.0	2.8	1.2	.15	.0023	8.1	3.1	4.7	.34	.023	.009	.011	.25	237
165.	733.	4.0	2.7	1.2	.15	.0023	8.1	3.1	4.6	.33	.023	.009	.011	.25	238
190.	705.	3.8	2.6	1.1	.14	.0023	8.1	3.0	4.4	.32	.023	.009	.011	.24	239
296.	624.	3.4	2.3	1.0	.13	.0023	8.1	2.8	3.7	.27	.022	.008	.009	.22	240
365.	590.	3.2	2.1	.9	.13	.0023	8.1	2.7	3.4	.25	.021	.007	.009	.22	241
671.	499.	2.7	1.7	.7	.11	.0023	8.1	2.4	2.6	.20	.020	.006	.007	.20	242
590.	519.	2.8	1.8	.8	.11	.0023	8.1	2.5	2.8	.21	.020	.006	.008	.20	243
401.	577.	3.1	2.1	.9	.12	.0023	8.1	2.7	3.3	.24	.021	.007	.009	.22	244
310.	622.	3.4	2.2	1.0	.13	.0023	8.1	2.8	3.6	.27	.022	.007	.009	.23	246
266.	649.	3.5	2.4	1.0	.14	.0023	8.1	2.9	3.9	.28	.022	.008	.010	.23	247
233.	675.	3.7	2.5	1.1	.14	.0023	8.1	2.9	4.1	.30	.022	.008	.010	.24	248
248.	666.	3.6	2.4	1.1	.14	.0023	8.1	2.9	4.0	.29	.022	.008	.010	.24	249
248.	668.	3.6	2.4	1.1	.14	.0023	8.1	2.9	4.0	.29	.022	.008	.010	.24	250
266.	657.	3.6	2.4	1.0	.14	.0023	8.1	2.9	3.9	.29	.022	.008	.010	.23	251
389.	598.	3.3	2.1	.9	.13	.0024	8.1	2.8	3.4	.25	.022	.007	.009	.22	252
540.	551.	3.0	1.9	.8	.12	.0024	8.1	2.6	3.0	.23	.021	.006	.008	.21	253
662.	526.	2.9	1.8	.8	.12	.0024	8.1	2.6	2.8	.21	.021	.006	.008	.21	254

Measured Mean Daily Discharge	Conduc- tivity µU/cm	Ca	Mg	Na	K	Fe	pH	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	F	NO <sub>3</sub>	B	SiO <sub>2</sub>	Day of Year
615.	539.	3.0	1.9	.8	.12	.0024	8.1	2.6	2.9	.22	.021	.006	.008	.21	255
515.	567.	3.1	2.0	.8	.12	.0024	8.1	2.7	3.1	.23	.021	.007	.008	.22	256
535.	565.	3.1	2.0	.8	.12	.0025	8.1	2.7	3.1	.23	.022	.007	.008	.22	257
794.	515.	2.8	1.8	.7	.12	.0025	8.1	2.6	2.7	.20	.021	.006	.008	.21	258
1110.	476.	2.6	1.6	.7	.11	.0026	8.1	2.5	2.3	.18	.020	.005	.007	.20	259
1220.	469.	2.6	1.6	.7	.11	.0026	8.1	2.5	2.3	.18	.020	.005	.007	.20	260
1230.	472.	2.6	1.6	.7	.11	.0026	8.1	2.5	2.3	.18	.020	.005	.007	.20	261
1180.	481.	2.7	1.6	.7	.11	.0027	8.1	2.5	2.4	.18	.021	.005	.007	.21	262
1060.	499.	2.8	1.7	.7	.11	.0027	8.1	2.6	2.5	.19	.021	.006	.007	.21	263
992.	512.	2.8	1.8	.7	.12	.0027	8.1	2.6	2.6	.20	.022	.006	.007	.21	264
1020.	513.	2.8	1.8	.7	.12	.0027	8.0	2.7	2.6	.20	.022	.006	.008	.22	265
1090.	510.	2.8	1.8	.7	.12	.0028	8.0	2.7	2.5	.20	.022	.006	.007	.22	266
1030.	522.	2.9	1.8	.7	.12	.0028	8.0	2.7	2.6	.20	.022	.006	.008	.22	267
902.	544.	3.0	1.9	.8	.12	.0028	8.0	2.8	2.8	.21	.023	.006	.008	.23	268
605.	603.	3.3	2.1	.9	.13	.0027	8.0	3.0	3.3	.25	.024	.007	.009	.24	269
466.	645.	3.6	2.3	1.0	.14	.0027	8.0	3.1	3.6	.27	.024	.008	.010	.25	270
397.	675.	3.7	2.5	1.0	.15	.0027	8.0	3.2	3.9	.29	.025	.008	.010	.26	271
357.	697.	3.9	2.5	1.1	.15	.0027	8.0	3.2	4.1	.30	.025	.008	.011	.26	272
334.	714.	4.0	2.6	1.1	.15	.0027	8.0	3.3	4.2	.31	.026	.009	.011	.27	273
286.	745.	4.1	2.8	1.2	.16	.0027	8.0	3.4	4.5	.33	.026	.009	.011	.27	274
245.	776.	4.3	2.9	1.3	.16	.0027	8.0	3.5	4.8	.35	.027	.010	.012	.28	275
221.	800.	4.4	3.0	1.3	.17	.0027	8.0	3.5	5.0	.36	.027	.010	.012	.28	276
215.	810.	4.5	3.0	1.3	.17	.0028	8.0	3.6	5.1	.37	.027	.010	.012	.29	277
210.	821.	4.5	3.1	1.4	.17	.0028	8.0	3.6	5.1	.37	.027	.010	.013	.29	278
202.	833.	4.6	3.1	1.4	.17	.0028	8.0	3.6	5.3	.38	.028	.010	.013	.29	279
178.	861.	4.8	3.3	1.4	.18	.0028	8.0	3.7	5.5	.40	.028	.011	.013	.30	280
154.	893.	5.0	3.5	1.5	.19	.0028	8.0	3.9	5.9	.43	.029	.012	.014	.31	281
128.	934.	5.2	3.7	1.6	.19	.0028	8.0	3.9	6.3	.45	.029	.012	.015	.32	282
108.	971.	5.4	3.8	1.7	.20	.0027	8.0	4.0	6.7	.47	.029	.013	.015	.32	283
94.	1005.	5.6	4.0	1.8	.20	.0027	8.0	4.0	7.0	.49	.030	.013	.016	.33	284
82.	1037.	5.7	4.1	1.9	.21	.0027	8.0	4.1	7.3	.51	.030	.014	.016	.33	285
74.	1063.	5.8	4.2	1.9	.21	.0027	8.0	4.1	7.5	.53	.030	.014	.017	.34	286
70.	1079.	5.9	4.3	2.0	.21	.0026	8.0	4.1	7.7	.54	.030	.014	.017	.34	287
72.	1078.	5.9	4.3	2.0	.21	.0027	8.0	4.2	7.7	.54	.030	.014	.017	.34	288
69.	1091.	6.0	4.4	2.0	.21	.0027	8.0	4.2	7.8	.54	.030	.014	.017	.34	289
65.	1107.	6.1	4.4	2.0	.22	.0027	8.0	4.2	7.9	.55	.030	.015	.018	.34	290
90.	1047.	5.8	4.2	1.9	.21	.0028	8.0	4.2	7.3	.51	.031	.014	.017	.34	291
140.	970.	5.5	3.8	1.7	.20	.0030	7.9	4.1	6.5	.47	.031	.013	.015	.33	292
147.	967.	5.5	3.8	1.7	.20	.0030	7.9	4.2	6.5	.46	.031	.013	.015	.34	293
393.	817.	4.6	3.0	1.3	.18	.0034	7.9	3.9	4.8	.36	.031	.010	.013	.32	294
172.	951.	5.4	3.7	1.6	.20	.0031	7.9	4.2	6.3	.45	.032	.012	.015	.34	295
163.	965.	5.5	3.8	1.7	.20	.0031	7.9	4.2	6.4	.46	.032	.013	.015	.34	296
160.	973.	5.5	3.8	1.7	.21	.0031	7.9	4.2	6.4	.46	.032	.013	.015	.34	297
134.	1008.	5.7	4.0	1.8	.21	.0030	7.9	4.3	6.8	.48	.032	.013	.016	.35	298
90.	1082.	6.0	4.3	1.9	.22	.0029	7.9	4.3	7.5	.53	.032	.014	.017	.35	299
79.	1109.	6.1	4.4	2.0	.22	.0028	7.9	4.3	7.8	.55	.032	.015	.018	.35	300
62.	1158.	6.3	4.6	2.1	.22	.0027	7.9	4.4	8.3	.58	.031	.015	.018	.36	301
49.	1205.	6.5	4.8	2.2	.23	.0026	8.0	4.4	8.8	.61	.031	.016	.019	.36	302
44.	1229.	6.6	5.0	2.3	.23	.0026	8.0	4.4	9.1	.62	.031	.016	.019	.36	303
39.	1255.	6.9	5.2	2.4	.24	.0026	8.0	4.5	9.6	.65	.032	.017	.020	.37	304
43.	1238.	6.8	5.1	2.4	.24	.0027	7.9	4.5	9.3	.64	.032	.017	.020	.37	305
44.	1236.	6.8	5.1	2.4	.24	.0027	7.9	4.5	9.3	.64	.032	.017	.020	.37	306
38.	1265.	7.0	5.2	2.4	.24	.0026	8.0	4.5	9.7	.66	.032	.017	.020	.37	307
32.	1301.	7.1	5.4	2.6	.24	.0026	8.0	4.5	10.1	.69	.032	.018	.021	.37	308
37.	1274.	7.0	5.3	2.5	.24	.0026	7.9	4.5	9.8	.67	.032	.017	.021	.37	309
43.	1248.	6.9	5.1	2.4	.24	.0027	7.9	4.5	9.4	.65	.032	.017	.020	.37	310
37.	1277.	7.0	5.3	2.5	.24	.0026	7.9	4.6	9.8	.67	.032	.017	.021	.37	311
32.	1306.	7.2	5.5	2.6	.25	.0026	8.0	4.6	10.1	.69	.032	.018	.021	.38	312
32.	1308.	7.2	5.5	2.6	.25	.0026	8.0	4.6	10.1	.69	.032	.018	.021	.38	313
34.	1298.	7.1	5.4	2.5	.24	.0026	7.9	4.6	10.0	.69	.032	.018	.021	.38	314
25.	1357.	7.4	5.7	2.7	.25	.0025	8.0	4.6	10.8	.73	.032	.018	.022	.38	316
22.	1383.	7.5	5.9	2.8	.25	.0024	8.0	4.6	11.1	.75	.032	.019	.023	.38	317
18.	1421.	7.7	6.1	2.9	.26	.0023	8.0	4.6	11.6	.78	.031	.019	.023	.38	318
17.	1433.	7.8	6.1	3.0	.26	.0023	8.0	4.6	11.7	.79	.031	.020	.024	.38	319
15.	1459.	7.9	6.3	3.0	.26	.0023	8.0	4.6	12.1	.81	.031	.020	.024	.38	320
14.	1473.	8.0	6.4	3.1	.26	.0023	8.0	4.6	12.2	.82	.031	.020	.024	.38	321
12.	1503.	8.1	6.5	3.2	.26	.0022	8.0	4.6	12.6	.84	.030	.021	.025	.38	322
12.	1504.	8.1	6.5	3.2	.26	.0022	8.0	4.6	12.6	.84	.031	.021	.025	.39	323
6.	1644.	8.7	7.3	3.7	.27	.0019	8.0	4.5	14.5	.96	.029	.023	.028	.39	324
6.	1644.	8.7	7.3	3.7	.27	.0019	8.0	4.5	14.5	.96	.029	.023	.028	.39	325
6.	1659.	8.8	7.4	3.7	.28	.0020	8.0	4.5	14.7	.97	.029	.023	.028	.39	326
6.	1645.	8.7	7.3	3.7	.27	.0019	8.0	4.5	14.5	.96	.029	.023	.028	.39	327
6.	1660.	8.8	7.4	3.7	.28	.0020	8.0	4.5	14.7	.97	.029	.023	.028	.39	328
6.	1662.	8.8	7.4	3.7	.28	.0020	8.0	4.5	14.7	.97	.029	.023	.028	.39	329
6.	1639.	8.7	7.3	3.7	.27	.0019	8.0	4.5	14.5	.95	.029	.023	.027	.38	330
7.	1628.	8.7	7.2	3.6	.27	.0020	8.0	4.5	14.2	.94	.030	.023	.027	.39	331
9.	1573.	8.4	6.9	3.4	.27	.0021	8.0	4.6	13.5	.90	.030	.022	.026	.39	332
9.	1576.	8.5	6.9	3.4	.27	.0021	8.0	4.6	13.6	.90	.030	.022	.026	.39	333
8.	1598.	8.5	7.1	3.5	.27	.0021	8.0	4.6	13.8	.92	.030	.022	.027	.39	334
8.	1610.	8.6	7.1	3.5	.27	.0021	8.0	4.6	14.0	.92	.030	.022	.027	.39	335
8.	1603.	8.6	7.1	3.5	.27	.0021	8.0	4.6	13.9	.92	.030	.022	.027	.39	336
6.	1667.	8.9	7.5	3.7	.28	.0020	8.0	4.5	14.8	.97	.030	.023	.028	.39	337
6.	1661.	8.8	7.4	3.7	.28	.0020	8.0	4.5	14.7	.97	.029	.023	.028	.39	338
6.	1676.	8.9	7.5	3.8	.28	.0020	8.0	4.6	14.8	.98	.030	.023	.028	.39	339
6.	1669.	8.9	7.5	3.7	.28	.0020	8.0	4.6	14.8	.97	.030	.023	.028	.39	340

Measured Mean Daily Discharge	Conductivity $\mu\text{S}/\text{cm}$	Ca	Mg	Na	K	Fe	pH	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	F	NO <sub>3</sub>	B	SiO <sub>2</sub>	Day of Year
6.	1699.	9.1	7.6	3.8	.28	.0020	8.0	4.6	15.1	.99	.030	.024	.029	.40	341
8.	1627.	8.7	7.2	3.6	.28	.0021	8.0	4.7	14.1	.94	.031	.023	.027	.40	342
12.	1554.	8.4	6.8	3.3	.27	.0023	8.0	4.7	13.1	.88	.032	.021	.026	.40	343
20.	1460.	8.0	6.3	3.0	.27	.0025	7.9	4.8	11.9	.80	.033	.020	.024	.40	344
18.	1484.	8.1	6.4	3.1	.27	.0025	7.9	4.8	12.2	.82	.033	.020	.025	.40	345
22.	1451.	8.0	6.2	3.0	.27	.0026	7.9	4.8	11.7	.79	.033	.020	.024	.40	346
21.	1463.	8.0	6.3	3.0	.27	.0026	7.9	4.8	11.9	.80	.033	.020	.024	.40	347
20.	1477.	8.1	6.3	3.0	.27	.0025	7.9	4.9	12.0	.81	.033	.020	.024	.41	348
18.	1502.	8.2	6.5	3.1	.27	.0025	7.9	4.9	12.3	.83	.033	.021	.025	.41	349
17.	1518.	8.3	6.6	3.2	.27	.0025	7.9	4.9	12.5	.84	.033	.021	.025	.41	350
17.	1524.	8.3	6.6	3.2	.28	.0025	7.9	4.9	12.6	.85	.033	.021	.025	.41	351
18.	1516.	8.3	6.5	3.1	.28	.0025	7.9	4.9	12.5	.84	.034	.021	.025	.41	352
21.	1491.	8.2	6.4	3.1	.27	.0026	7.9	5.0	12.1	.82	.034	.021	.025	.41	353
22.	1486.	8.2	6.4	3.0	.27	.0026	7.9	5.0	12.0	.81	.034	.020	.025	.41	354
23.	1482.	8.2	6.3	3.0	.27	.0027	7.9	5.0	12.0	.81	.034	.020	.025	.43	355
23.	1487.	8.2	6.4	3.0	.28	.0027	7.9	5.0	12.0	.81	.035	.020	.025	.42	356
23.	1491.	8.2	6.4	3.0	.28	.0027	7.9	5.0	12.0	.82	.035	.021	.025	.42	357
20.	1526.	8.4	6.6	3.2	.28	.0026	7.9	5.0	12.5	.84	.035	.021	.025	.42	358
20.	1532	8.4	6.6	3.2	.28	.0026	7.9	5.1	12.5	.85	.035	.021	.025	.42	359
18.	1560.	8.6	6.8	3.3	.28	.0026	7.9	5.1	12.9	.87	.035	.022	.026	.43	360
17.	1578.	8.7	6.9	3.3	.29	.0026	7.9	5.1	13.1	.88	.035	.022	.026	.43	361
18.	1570.	8.7	6.8	3.3	.29	.0026	7.9	5.1	13.0	.87	.035	.022	.026	.43	362
18.	1576.	8.7	6.8	3.3	.29	.0026	7.9	5.1	13.0	.88	.035	.022	.026	.43	363
18.	1581.	8.7	6.9	3.3	.29	.0027	7.9	5.2	13.1	.88	.035	.022	.026	.43	364
21.	1551.	8.6	6.7	3.2	.29	.0027	7.9	5.2	12.7	.86	.036	.021	.026	.43	365

Table A10-1. Conductivity simulated from flow records for the Henry's Fork River for the water year beginning October 1, 1971.

Day of Year	Measured	Predicted	Simulated	Day of Year	Measured	Predicted	Simulated	Day of Year	Measured	Predicted	Simulated
1	1560	1403	1555	31	1230	1257	1337	61	1310	1271	1034
2	1540	1401	1394	32	1200	1252	1330	62	766	1251	1237
3	1550	1404	1307	33	1180	1265	1186	63	1150	1243	1237
4	1590	1406	1295	34	1340	1290	1334	64	1100	1249	1412
5	1530	1409	1339	35	1340	1313	1358	65	1130	1263	1450
6	1540	1397	1198	36	1310	1263	1117	66	1180	1254	1242
7	1580	1356	1283	37	1200	1235	1219	67	965	1232	1285
8	1510	1336	1358	38	1190	1220	1251	68	960	1218	1340
9	1500	1318	1220	39	1230	1221	1302	69	878	1207	1109
10	1460	1299	1418	40	1170	1244	1083	70	1110	1206	1322
11	1520	1280	1499	41	1180	1214	924	71	1080	1216	1231
12	1380	1300	1507	42	1160	1290	1261	72	1200	1215	1053
13	1300	1292	1187	43	1360	1277	1077	73	1270	1224	1221
14	1300	1290	1051	44	1220	1258	979	74	1300	1233	1292
15	1460	1295	1007	45	1300	1395	1026	75	1300	1258	1321
16	1650	1301	1132	46	1290	1387	1152	76	1370	1278	1265
17	1350	1296	1268	47	1340	1266	1224	77	1370	1309	1594
18	1430	1298	1445	48	1340	1272	1138	78	1300	1303	1623
19	1350	1298	1443	49	1200	1298	996	79	1300	1297	1657
20	1360	1292	1409	50	1200	1279	1114	80	1310	1310	1489
21	1320	1304	1287	51	1250	1287	925	81	1370	1330	1760
22	1360	1278	1446	52	1310	1222	1233	82	1380	1339	1484
23	1370	1264	1255	53	1310	1202	1288	83	1370	1343	1372
24	1350	1271	1344	54	1210	1219	1236	84	1270	1336	1479
25	1350	1265	1294	55	1200	1189	1253	85	1220	1324	1177
26	1360	1313	1331	56	1030	1116	1303	86	1230	1308	1074
27	1220	1334	1315	57	1030	1146	1178	89	1240	1304	1120
28	1210	1341	1350	58	1260	1210	1130	90	1230	1298	1271
29	1210	1310	1393	59	1270	1291	1055	91	1190	1292	1120
30	1210	1275	1437	60	1310	1281	1029	92	1230	1285	1123

<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>	<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>	<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>
93	1160	1307	1083	148	1120	1214	1277	204	1130	787	602
94	1180	1320	1169	149	1110	1209	1296	205	1010	738	613
95	1140	1346	1079	150	1280	1228	1288	206	1020	782	617
96	1120	1375	1208	151	1280	1244	1327	207	889	785	649
97	1150	1394	1121	152	1280	1256	1237	208	956	819	696
98	1150	1414	1093	153	1260	1256	1301	209	954	838	687
99	1150	1428	1106	154	1180	1238	1222	210	986	850	697
100	1160	1408	1126	155	1150	1238	1341	211	994	849	613
101	1130	1397	1221	156	1090	1256	1284	212	975	848	721
102	1130	1394	1219	157	1080	1270	1581	213	931	883	847
103	1130	1383	1384	158	1120	1257	1738	214	875	859	832
104	1120	1373	1546	159	1120	1229	1532	215	875	733	914
105	1110	1337	1335	160	1100	1202	2042	216	806	810	916
106	1100	1307	1327	161	1100	1180	1940	217	822	792	937
107	1110	1279	1189	162	1100	1149	1688	218	817	792	806
108	1120	1175	1228	163	1110	1118	1689	219	890	782	942
109	1380	1093	1094	164	979	1112	1540	220	903	749	970
110	1060	1008	980	165	924	1121	1754	221	905	776	955
111	759	930	920	166	919	1108	1434	222	985	761	959
112	832	946	977	167	906	1091	1596	223	898	787	857
113	844	996	920	168	1060	1107	1690	224	841	796	838
114	1150	1044	1006	169	965	1116	1778	225	842	771	756
115	1160	1068	1231	170	1020	1094	1705	226	843	750	658
116	1170	1067	1195	171	979	1077	1622	227	768	744	772
117	1370	1079	1513	173	1020	1028	1440	228	729	719	799
118	1030	1063	1331	174	1040	946	1036	229	715	693	670
119	1000	1061	1289	175	826	881	806	230	764	718	631
120	1000	1066	1194	176	618	800	749	231	809	739	655
121	898	1071	1294	177	713	760	648	232	868	763	625
122	898	1101	1050	178	792	707	598	233	898	768	534
123	899	1127	1048	179	613	773	689	234	922	789	578
124	909	1148	1182	180	759	784	677	235	872	763	756
125	913	1175	1242	181	827	831	711	236	905	728	655
126	1040	1194	1317	182	806	973	787	237	905	739	768
127	1150	1202	1236	183	814	1083	1219	238	800	733	723
128	1270	1215	1164	184	919	1121	1231	239	665	705	800
129	1180	1180	1219	185	947	1100	1182	240	516	624	690
130	1350	1149	1240	186	906	1098	1316	241	642	590	706
131	1240	1122	1213	187	994	1100	1231	242	645	499	550
132	1240	1119	1136	188	1070	1063	1131	243	580	519	639
133	1080	1109	1210	189	968	1042	962	244	638	577	711
134	1170	1094	1061	190	980	1068	1028	246	674	622	823
135	937	1085	1180	191	877	1045	961	247	675	649	676
136	1000	1083	1190	192	955	1042	1023	248	704	675	619
137	907	1089	1184	193	832	1036	886	249	690	666	618
138	929	1099	1041	194	890	1010	954	250	670	668	503
139	931	1115	1014	195	869	1018	964	251	606	657	521
140	1080	1140	1296	196	892	1006	868	252	531	598	426
141	1090	1150	1098	197	868	1003	823	253	497	551	372
142	1130	1163	1216	198	852	997	723	254	510	526	337
143	1100	1188	1465	199	855	988	937	255	504	539	349
144	1140	1218	1278	200	815	984	728	256	524	567	470
145	1210	1247	1755	201	715	912	693	257	505	565	472
146	1210	1246	1726	202	941	889	727	258	506	515	547
147	1210	1235	1554	203	1060	892	646	259	518	476	448



<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>	<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>	<u>Day of Year</u>	<u>Measured</u>	<u>Predicted</u>	<u>Simulated</u>
260	471	540	469	295	900	1013	951	331	1610	1628	1479
261	449	500	472	296	897	1124	965	332	1620	1573	1636
262	414	542	481	297	905	973	1050	333	1590	1576	1369
263	410	535	499	298	904	1008	1018	334	1610	1598	1500
264	471	453	512	299	968	1082	1162	335	1620	1610	1408
265	402	420	513	300	1020	1109	1043	336	1610	1603	1330
266	387	418	510	301	1060	1158	1046	337	1610	1667	1375
267	390	492	522	302	1340	1205	1124	338	1690	1661	1786
268	521	465	544	303	1140	1229	1157	339	1700	1676	1965
269	467	483	603	304	1140	1255	1102	340	1720	1669	1813
270	514	592	645	305	1150	1238	1196	341	1810	1699	1621
271	600	657	675	306	1200	1236	1218	342	1330	1627	1561
272	600	692	697	307	1210	1265	1160	343	1340	1554	1463
273	661	775	714	308	1210	1301	1222	344	1450	1460	1285
274	698	826	745	309	1180	1274	1132	345	1430	1484	1639
275	730	738	776	310	1170	1248	900	346	1400	1451	1929
276	742	695	800	311	1210	1277	1161	347	1400	1463	1630
277	752	607	810	312	1220	1306	1361	348	1440	1477	1668
278	756	791	821	313	1180	1308	1320	349	1440	1502	1625
279	758	800	833	314	1180	1298	1374	350	1470	1518	1602
280	373	824	861	316	1140	1357	1469	351	1510	1524	1716
281	818	758	893	317	1280	1383	1353	352	1510	1516	1602
282	918	931	934	318	1250	1421	1343	353	1490	1491	1913
283	978	979	971	319	1290	1433	1336	354	1490	1486	1649
284	978	1095	1005	320	1320	1459	1493	355	1380	1482	1451
285	1050	1079	1037	321	1340	1473	1245	356	1380	1487	1261
286	1050	1172	1063	322	1340	1503	1145	357	1380	1491	1182
287	1090	1492	1079	323	1540	1504	1327	358	1380	1526	1314
288	1100	1275	1078	324	1540	1644	1639	359	1480	1532	1336
289	1130	1182	1091	325	1580	1644	1720	360	1470	1560	1290
290	1120	1120	1107	326	1570	1659	1460	361	1470	1578	1156
291	1060	922	1047	327	1570	1645	1363	362	1530	1570	1316
292	821	993	970	328	1580	1660	1637	363	1530	1576	1402
293	840	874	967	329	1570	1662	1708	364	1530	1581	1400
294	712	770	817	330	1660	1639	1551	365	1530	1551	1569

KEY WORDS: Time series, mathematical modeling, dissolved solids, water chemistry, salinity, conductivity, water quality, streamflow.

Abstract: The potential for obtaining information concerning certain water quality variables on a stream by considering the relationships which exist between quality and quantity variables is examined. More precisely, the study is concerned with the relationship which exists between discharge and inorganic water quality in natural streams. Inorganic water quality is taken to refer to the concentrations of inorganic constituents found dissolved in the stream water. Natural streams are defined as those streams which are free of man's influence although some compromise of this definition is necessary in actual application. The relationship studied is the negative correlation between inorganic water quality and

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discharge which is found in virtually all streams. Study is limited to thirteen inorganic constituents. A relationship between constituent concentrations and conductivity based on chemical theory is developed and is applicable to any stream sample. Applications are made using data from five streams.

Reference: Lane, William L., Colorado State University, Hydrology Paper No. 73 (June 1975) "Extraction of Information on Inorganic Water Quality.

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