THESIS

WATER QUALITY ASSESSMENT WITH ROUTINE MONITORING DATA

Submitted by

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ABSTRACT OF THESIS

WATER QUALITY ASSESSMENT WITH ROUTINE MONITORING DATA

Federal legislation in recent years has required the states to develop water quality management programs which include stream standards and river monitoring. Water quality data, routinely collected by state and federal agencies, has often been of little use in directly determining stream standards compliance. This problem is due to the discrepancy between the statistical nature of water quality sampling and nonstatistically expressed stream standards. However, the use of probability and statistical models in water quality analysis may provide useful assessments of river water quality with stream standards.

This research consists of the development and testing of five statistical procedures which allow river water quality to be assessed from available, routinely collected data. The procedures include: 1) probability density function modeling of water quality variables, 2) multiple linear regression modeling of water quality variables, 3) conditional probability modeling of stream standard violations given known river conditions, 4) a water quality index indicating changes in water quality, and 5) a water quality index indicating compliance/noncompliance of water quality variables with stream standards. The utility of each procedure is illustrated with a case study.

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INTRODUCTION

1.1 Background

Effective water quality management programs, capable of maintaining acceptable river water quality, are becoming more important as the stresses placed upon water resources increase. With the nation's population continuing to move westward into regions already critically short of water, the multiple use of water for agricultural, mining, recreational, and municipal uses will become widespread. The relatively plentiful waters of the eastern United States, which have been burdened for years with the wastes of cities and industry, are now recognized to be facing contamination from hazardous wastes. Federal, state, and local governments have produced legislation in response to environmental awareness, and large public expenditures have been made in the development of water quality management programs. A major function of the regulatory agencies, which have been established to manage water quality, is to monitor surface waters and evaluate water quality information with respect to the goals set forth by legislative action. It is apparent, that as we move into the twenty-first century, the ability of water quality management agencies to assess and predict the suitability of water for various uses is becoming a very critical concern.

The capability of management agencies, however, to make such evaluations has not been well developed. A fundamental problem encountered by management has been the meaningful evalution of water quality samples collected from stochastic water quality processes. Management agencies must evaluate dynamic water quality conditions with samples which do not necessarily include information pertinent to management objectives. For example, data collected by routine monitoring networks, which typically sample infrequently, contain little information regarding the occurrence of stream standard violations. This results because, often, violations represent short-term episodes which will not be detected unless a sample happens to be collected precisely at the time of occurrence. If a principal management objective is the detection of stream standard violations, little information pertaining directly to the objective may be expected from this type of water quality data.

It may be possible, however, for water quality management agencies to make useful inferences about water quality processes from sample information by following examples provided by other disciplines which deal with stochastic systems. For example, the closely related science of hydrology has long considered the occurrence of floods to be a stochastic phenomena. Statistical procedures have been developed to extrapolate information regarding flood frequencies. This statistically derived information is then used as a basis for decision making. By recognizing the parallel between quantity and quality behavior, the water quality management profession could incorporate methodologies developed for stochastic processes into analytical procedures for the assessment of water quality. This analytic approach will provide inferences on water quality, in general, from water quality samples. In so doing, the information derived from the monitoring program will more directly relate to management goals.

1.2 Objective

The objective of this research is to develop analytical procedures which provide information relevant to water quality management needs from routinely collected data. To meet this objective, typical water quality management programs, consisting of river monitoring (data collection) and stream standards (management goals), are identified to provide a basis for the design of useful analytical procedures. Procedures are then developed which utilize commonly available water quality data and provide evaluations of management goals by applying basic probability and statistical techniques.

The work presented in this report is limited to the initial development of five analytical procedures and a case study illustrating the applicability of each. Specifically, the five procedures consist of: 1) probability modeling of individual water quality constitutents whereby a criterion is suggested for the selection of an appropriate probability density function based on sample coefficient of skew, 2) multiple linear regression modeling of individual water quality constitutents based on known river conditions, 3) conditional probability modeling (given known river conditions) of stream standard violations, 4) an index indicating changes in water quality using hypothesis testing theory, and 5) an index indicating the suitability of river water for specific uses as defined by stream standards.

1.3 Scope

Techniques suggested in the report are developed and tested using water quality data collected by the U.S. Geological Survey and by the states of Colorado, Oregon, Illinois, and Maryland. A statistical, rather than physical modeling approach was chosen due to the multidimensionality and complexity of water quality processes. If a physical modeling approach had been taken, several different models would have been needed to adequately simulate the various types of constituent behavior, i.e., point source vs. nonpoint source and conservative vs. nonconservative pollutants. Using the statistical approach, a more simple task of calibrating the same analytical models to each constituent was all that was necessary.

The five procedures used in this work represent only a few of many possible statistical approaches for the evaluation of water quality from routinely collected data. They were chosen to provide an example of how water quality management agencies may effectively utilize commonly available data. For this reason, procedure derivations presented in the report are not rigorous mathematical exercises intended to be universally applicable. They are, rather, simple descriptions of the application of basic statistical techniques into procedures for the evaluation of commonly available water quality data. References are cited in the text for more complete descriptions of the fundamental techniques employed by each procedure.

1.4 Definitions

Water quality is defined in this report as a general statement regarding the various chemical, biological, and physical characteristics of river water. Water quality programs refer to efforts made by state and federal agencies to monitor, evaluate, and improve water quality. Stream standards contain criteria adopted by a state which define threshold levels of acceptable/nonacceptable water quality constituent concentrations for specific beneficial uses. Stream standard violations occur when the concentration of water quality variables exceeds designated stream standard concentrations. Water quality constituents will be referred to as variables rather than parameters in this work to avoid confusion between variables and statistical parameters. The convention of expressing water quality constituents as variables is well suited for statistical analysis because the constituents are, indeed, the random variables modeled by the statistical procedures.

Water quality monitoring is defined as the collection of river water quality information. The most common types of water quality monitoring networks are fixed station/fixed frequency monitoring and synoptic survey monitoring. Fixed station/fixed frequency monitoring usually consists of an ongoing program where samples are collected at a relatively constant interval at a permanently located station. The samples are generally analyzed for several chemical constituents and a few biological indicators and represent a statistical sampling of realizations from a population. Synoptic survey monitoring, sometimes called intensive survey monitoring, differs from fixed station/fixed frequency monitoring in the time and space domain. This type of monitoring is commonly performed over an entire river reach for a specified interval. Synoptic surveys often include biologic assays and hydrologic studies as well as chemical analyses.

The expression "general assessment" is used frequently in the report and is defined as a quantitative statement about water quality with respect to stream standards. General assessments of river water quality are suggested rather than simply determining compliance or noncompliance of individual samples with stream standards. The utility of making general assessments of water quality results from the summarization of a large amount of information regarding the behavior of an individual constituent. Assessments contain information extrapolated through statistical modeling which may be used as a basis of comparison of water quality from year to year or between different rivers. The use of general water quality assessments suggest a river monitoring emphasis of information summarization and comparison rather than stream standard compliance enforcement. As pointed out in following sections, the task of information summarization is a more suitable objective of routine monitoring than compliance enforcement.

1.5 Organization of Report

The concluding portion of this chapter contains a survey of current literature pertaining to statistical analysis of water quality data. Chapter 2 reviews current state stream standards and monitoring practices to identify the goals and the means of attaining the goals of state water quality programs. With this background, Chapter 3 suggests analytical procedures designed for typical water quality data which may provide assessments in accordance with state stream standards. Chapter 4 presents an illustration of the techniques applied to the Little Wabash River in Illinois. In Chapter 4, the results of the analysis are compared to a daily record of water quality to gain insight into the usefulness of each procedure. Chapter 5 presents summary, conclusions, and recommended areas of further research. The appendices present the results of two studies related to the principle topics of this report.

1.6 Review of Literature

Numerous papers have been published in the area of water quality management in recent years. Very complete reviews of literature have been presented in the Ph.D. dissertations of Sanders (1974) and Loftis

(1978) concerning current research and more specifically monitoring network design. A very good general background of water quality hydrology is provided by Velz (1970) and Hem (1970). The specific area of statistical analysis of routine water quality data has not received a great deal of attention in the literature. This review will present literature concerning the goals and problems associated with water quality management and the statistical analysis of water quality data.

Even before the passage of federal legislation requiring states to adopt stream standards, a few states including California were attempting to establish water quality criteria. Pomeroy and Orlob (1967) describe in a California State Water Quality Commission publication problems associated with limiting concentration-type stream standards, problems which are still being addressed today.

> To the lay person who has not been faced with the administrative problems of enforcing standards, it may appear that setting a standard for a particular situation would be accomplished merely by stating one numerical value representing the extreme allowable value of that indicator. Several questions, however, may arise. Is the limit a figure that shall not be exceeded at any time, or not exceeded as a median, or as an average? If it is an average, over what period of time shall the average be taken? If it is not to be exceeded at any time, what happens if it is exceeded once? What allowances are made for analytical errors? If the standard for a certain constituent is "none" how small an amount does that really mean?

Current stream standards documents rarely deal specifically with these questions, rendering the standards somewhat vague and impractical. This lack of practical definition common in stream standards prompted Sanders and Ward (1978) to state

> ...it is easy to see why water quality data often plays little or no role in the daily operations of a water quality management agency.

Minton (1980) looked at the current management structure in the light of the overall management objective of protecting the quality of receiving waters and their beneficial uses. One of his conclusions was that new concepts for stream standards need to be developed whereby the objectives of water quality management may be attained. It is pointed out that as standards exist today they, "often imply a deterministic certainty in an uncertain world." He also states that it must be recognized that stream standards will never be sufficient by themselves to protect beneficial uses. Land use activities must be understood and improved to achieve desired water quality levels.

A report issued by the United States General Accounting Office (U.S. General Accounting Office, 1981, Vol. I), was very critical of current monitoring efforts conducted by state and federal water quality data collection agencies. The report suggests that fixed station/fixed frequency monitoring networks cannot provide information necessary for relevant water quality assessments. The GAO recommends that such monitoring be discontinued immediately and replaced by synoptic survey monitoring. Synoptic survey monitoring has been performed on a very limited basis, according to the U.S. Geological Survey and the U.S. Environmental Protection Agency (U.S. General Accounting Office, 1981, Vol. II), due to problems associated with cost and areal extent of information. An excellent example of a synoptic survey may be found, however, in a series of Geological Survey Circulars (U.S. Geological Survey 1975, 1976). In this work, an extensive study of the Willamette River Basin in Oregon is described.

Most of the problems identified by the GAO report are legitimate, but the conclusion of discontinuing cost effective fixed station/fixed frequency sampling in favor of synoptic surveys is questionable. A large amount of research has been devoted to the development of rational monitoring network design procedures and through the use of well designed networks and appropriate analytical techniques, general water quality may be evaluated with fixed station/fixed frequency data.

A Colorado State University short course manual edited by Sanders (1980) describes the state-of-the-art of water quality monitoring network design. This report outlines very specifically rational design procedures which enable the development of monitoring networks able to produce data useful for the objectives designated by water quality management agencies. A full range of topics are covered including sampling location, sampling frequency, and statistical analysis of water quality data. The design of a monitoring network based on rational considerations is a fundamental first step in acquiring the capability of meaningful water quality assessment.

The accurate and consistent analysis of water quality samples is another primary concern. Simpson (1980) describes how accuracy and consistency of water quality data are maintained in the United Kingdom. The author summarizes the principle ambition of the British program as follows. "The central feature of the Harmonized Monitoring Scheme is that the analytical results shall be of demonstrated accuracy." Analytical accuracy is determined by a rigorous inter-laboratory calibration procedure whereby different laboratories cross-check each other to assure acceptably accurate sample evaluations. Included in the program is the specific definition of goals and a clear description of sampling procedures. The author points out that the operation of such a monitoring system is "a major undertaking" but emphasizes the need for accurate and reliable water quality information.

Once water quality data is assumed to be of acceptable accuracy the problem becomes what analytical procedures should be selected to provide information from the data. Ward (1979) describes two general levels of data analysis. First, the most general approach is the use of statistics and indices for water quality assessment in time and space. Ponce (1980) provides an excellent summary of statistical procedures commonly used in water quality data evaluation. Ott (1978) and Landwehr (1979) present reviews of water quality indices developed over the past several years. Secondly, according to Ward (1979), specific water quality problems may prompt the use of time series analysis and/or physical modeling of water quality processes. Wakeford and Knowles (1978) also suggest the use of time series analysis and physical models to enhance water quality management programs. An extensive review of existing hydrologic and water quality models is provided by Cembrowicz et al. (1978).

Descriptions of logical statistical sequences for the analysis of water quality data are not common in the literature. Alther (1979) describes a statistical sequence used to evaluate a stream contaminated with effluent from a sewage treatment plant. Routine water quality data was used in the analysis. Cluster analysis was used to discern differences in the stream as compared to other rivers in the area. Decreasing pollutant concentration with increasing distance downstream of the effluent source was statistically shown with linear regression analysis. A trimmed "t" test was used to determine two populations with different mean concentrations of iron. The author concluded that the use of statistical tests "greatly facilitated the interpretation of the data."

Wentz and Steele (1980) used statistical procedures to assess the impact of mining activity on the Yampa River system. Annual river temperature fluctuation was analyzed with a harmonic-analysis procedure. This technique may allow the assessment of future temperature changes. Trends in specific conductance were identified using Kendall's tau nonparametric test with flow-adjusted annual means. Site specific relationships were developed to predict major ion concentration from specific conductance records.

Lane (1975) used linear regression analysis to disaggregate specific conductance into major ion concentration. The procedure used in this research consisted of three steps. Specific conductance is estimated via a relationship determined between discharge and conductivity. Next, ion proportions are estimated from the estimate of specific conductance. Finally, total dissolved solids concentration is estimated in accordance with the estimated conductivity value and ion concentrations are then determined. Lane (1975) also added a stochastic component to the model to account for the random component of variable behavior.

Multiple linear regression models have been used to relate water quality characteristics to basin characteristics (U.S. Environmental Protection Agency, 1978). Generalized background levels of water quality were estimated by removing land use variables from the regression equation. It is concluded in the report that multiple regression modeling of water quality versus basin characteristics may be a useful screening technique to assess the effects of land use activities.

The use of probability distributions to model the behavior of water quality variables has been suggested by researchers (Sherwani and

Moreau, 1975; Sanders and Ward, 1978; and others). Sherwani and Moreau (1975) suggest the identification of underlying probability distributions to assist in monitoring network design. Sanders and Ward (1978) present the idea of stream standards based on probability distributions. The determination of a water quality variable's probability distribution, conditioned on known variables, was suggested by Loftis (1978) in his dissertation section devoted to recommended research.

Chapter 2

CURRENT STREAM STANDARDS AND MONITORING PRACTICES

2.1 Introduction

Due to federal water quality legislation, the states have been required to develop water quality standards on which to base the suitability of surface waters for specific uses and monitor those waters to ensure standards are being achieved. Because each state is responsible for its own standards and monitoring system, some diversity has developed among the fifty states. This chapter looks briefly at the federal legislation responsible for the current water quality management structure, the guidelines set forth by federal regulatory agencies, and the resulting stream standards and monitoring practices adopted by the states. The chapter is not a complete description of stream standards and monitoring practices but rather a general overview of water quality management systems practiced by the states. This review is provided to identify typical standards and monitoring practices, later chapters will use this information in the development of analytical procedures designed specifically for common management programs.

2.2 Background

Since the passage of the Clean Water Act, PL 89-234, in 1965, the states have been required by the federal government to establish water quality monitoring programs. According to the 1965 act, each state was to develop its own set of standards and monitor compliance by sampling the surface waters of the state. When a stream was found to be out of compliance, legal action could be taken against the party or parties that were responsible for the violation. This administrative system proved ineffectual, however, because it was often difficult to prove in court who was responsible for violations. In 1972, PL 92-500, The Federal Water Pollution Control Act Amendments, was passed by Congress and emphasis changed from stream standards to effluent standards. States were still required to have a set of stream standards but enforcement of water quality goals was now carried out through the control of waste discharges. Stream standards served as a partial basis for determining effluent limitations and, therefore, remained an integral part of the national water pollution control system.

Passage of PL 92-500 gave the Environmental Protection Agency responsibility to provide guidance in water quality regulation. Under this guidance from EPA, the states had to develop their own water quality management programs which were to include stream standards and a water quality monitoring scheme. State programs were subject to approval by the EPA and, if a state did not adopt a suitable plan, the EPA would establish a program for the state. To assist the states the EPA published guidelines which describe in some detail the minimum requirements of an acceptable water quality program (U.S. Environmental Protection Agency, 1976).

2.3 Survey of Current Standards and Monitoring

2.3.1 Stream Standards

Chapter 5 of the EPA publication, Guidelines for State and Areawide Water Quality Management Program Development (U.S. Environmental Protection Agency, 1976) enumerates the minimum contents of the state water quality standards document:

1. Certification that the standards are included within state law;
2. Statement of general policy consistent with 40 CFR Section 130.17;
3. Statement of applicability of water quality standards, including the state's mixing zone policy;
4. Definitions;
5. A listing of the use designations for all the waters of the state, including any site specific water quality criteria for specific segments;
6. Water quality criteria that define the conditions necessary to maintain the beneficial water use designations;
7. An antidegradation statement;
8. Specifications of statistical requirements and reference to analytical testing and sampling procedures to determine if standards are being met; and
9. A listing of outstanding national resource waters.

It is also suggested that provisions be made to deal with special flow conditions which include intermittent flow, low flow, high flow, and regulated flow.

Stream standard documents from each state, published in the Environment Reporter (U.S. Bureau of National Affairs, 1980), were reviewed and compared with the EPA guidelines. It was found that most standards documents are very similar in composition. Nearly all states have similar expressions of inclusion of stream standards in state law, general policy, applicability, definitions, and antidegradation. A set of narrative standards is commonly found which pertain to man-made wastes such as oil and grease. These standards generally apply to all waters and at all times. Most states list beneficial uses of water they wish to protect and have a set of specific criteria which apply to each use. The specific criteria are most frequently expressed as limiting concentrations never to be exceeded by individual water quality constituents. Many states reference Standard Methods for the Examination of Water and Waste Water, 14th Edition (American Public Health Association, 1975), apparently, to meet the EPA requirement of specifying statistical requirements and operational procedures. Most states define a low and/or high flow condition under which the standards do not apply. Basic differences occur among a few states in the wording of specific criteria and definition of critical high or low flow and these topics will be discussed in more detail.

2.3.1.1 Specific Criteria

Specific criteria and standards are established for each water quality variable considered important to a particular beneficial use. Specific criteria are generally written as a maximum or minimum concentration not to be exceeded. The level at which the standard is set represents the threshold concentration of the particular constituent where the suitability of the water is marginal. The determination of threshold values of water quality variable concentrations is a difficult task and to assist the states, the EPA has published values in the "Red Book" based on current scientific information (U.S. Environmental Protection Agency, 1977). Most states have adopted these EPA criteria into their stream standards.

Since water quality constituents behave as stochastic variables, the determination of compliance/noncompliance with limiting-concentration type stream standards is difficult. Unless samples are collected continuously, it can not be absolutely determined that this type of standard is being achieved at all times. For this reason, various states have established standards expressed in terms related to individual samples or in statistical terms applying to statistics calculated from a number of samples. These standards are designed to be directly applicable to information contained in routinely collected water quality data. A few examples will be cited here.

New Mexico expresses stream standards for several variables in a manner which acknowledges the fact that water quality variables are subject to random variation. The standards pertaining to dissolved oxygen, pH, and temperature are expressed as numeric limits not to be exceeded in any single sample. These criteria are similar to those used by most states except for the explicit instruction that the standard applies to any single sample. Many other states may imply the same interpretation but often they do not clearly explain their meaning. New Mexico standards of total dissolved solids, sulfate, and chlorides are expressed as monthly average concentrations not to be exceeded.

Oklahoma has established stream standards at particular sampling locations for total dissolved solids, sulfate, and chlorides in terms of the historical mean and standard deviation of each variable. These standards are expressed such that the yearly arithmetic mean concentration is not to exceed the historical mean plus one standard deviation. They further state that not more than one sample in twenty may exceed the historical mean plus two standard deviations. Standards pertaining to other variables are expressed as simple limits not to be exceeded.

South Dakota stream standards allow some variation above the specified criteria for each constituent. The criteria for each variable refer to one of three acceptable levels of variation defined in the standards document. The first acceptable amount of variation applies to most constituents including nearly all metals. These standards are to be maintained at all times. The second applies to ammonia and specifies that the standard is to be maintained at all times based on a twenty-four hour representative composite sample. Also the numeric value of any one grab sample may not exceed 1.75 times the standard. The third allowable level of variation found in South Dakota standards applies to total dissolved solids, sulfate, and chlorides and states that the standard is to be maintained at all times based on the average of five consecutive twenty-four hour composite samples. In addition the numerical value of any one sample may not exceed 2.0 times the standard.

Texas expresses most of its stream standards in terms of annual mean concentration. The standards document also states that whenever an unusual chemical concentration is found an investigation will be made to determine its cause. This policy is fairly unique among the states and would seem to be quite useful. Texas, as well as various other states, recognizes the natural diurnal variation of dissolved oxygen in standards applying to that variable. The Texas standards allow a one milligram per liter fluctuation below the D.O. criteria for not more than eight hours during any twenty-four hour period.

2.3.1.2 Flow Exception Policies

Section 5.8 of Guidelines for State and Areawide Water Quality Management Program Development (1976) states that water quality standards should protect water quality in critical high and low flow situations. It further indicates that effluent limitations designed to maintain stream standards may be based on design low and high flows. It follows from this statement that stream standards do not necessarily apply to flows beyond the design criteria. Most states, however, do not include a design high flow in their stream standards. This may result from the fact that nonpoint source pollution is primarily affected by high flows and these sources are not included in the effluent permit system (National Pollution Discharge Elimination System). The state of Washington is one of the few states which makes an explicit statement regarding high flows. The total dissolved gas standard does not apply to flows greater than the seven-day average high flow expected to occur an average of once in ten years. Louisiana includes a statement to the effect that standards do not apply when natural conditions cause exceedance. This statement may be construed to be a high flow statement but would appear to be difficult to implement.

Low flow statements occur more frequently in state stream standards. Periods of low stream flow often create problems with respect to point discharges due to decreased dilution capabilities of the receiving stream. Nonpoint source pollution is not generally a problem during low flow periods because of little surface runoff contributing to total stream flow. A low flow design criteria commonly used in stream standards is the seven-day average low flow expected to occur an average of once in ten years (7Q10). The use of the 7Q10 seems to result from the use of this criteria in the design of sewage treatment plants. Four states specify in their stream standards that waste discharge plants are to be designed for the 7Q10 and make no mention of relaxing standards during periods of critical low flow. Other states, numbering at least twenty-one, make the blanket statement that specific numeric criteria do not apply during periods of flow less than the 7Q10. Five states relax their standards for some but not all water quality variables at this same discharge. New Hampshire and Tennessee use a ten-day, twenty-year flow and a three day, twenty year flow design criteria, respectively, below which their specific standards do not apply. South Dakota uses two design discharges, the seven-day, twenty-five year flow for high quality waters and the seven-day, five-year flow for low quality waters. Texas relaxes its dissolved oxygen standard at the seven-day, two-year flow.

Little documentation is available in the literature regarding the frequency and duration of design low flows. For this reason, three design low flows were calculated for six rivers in the United States and the frequency and duration of each determined. A brief summary of this research may be found in Appendix A.

2.3.1.3 Data Requirements

The amount and type of data necessary to determine compliance with stream standards is dependent upon the manner in which the standards are expressed. Statistically based stream standards, employed by a few states, implicitly suggest the data requirements of these states. For example, standards expressed as mean annual concentrations require data which will provide acceptably accurate estimates of annual means, standards written for 24-hour composite samples require samples to be drawn around the clock, etc. The commonly used limiting-concentration type stream standard requires continuous monitoring for strict compliance enforcement. State stream standards documents which include flow exception policies require discharge measurements as well as quality measurements to be made.

2.3.2 Monitoring Networks

The collection of river water quality information is conducted by federal and state agencies with the principal responsibility belonging to the states. The Code of Federal Regulations (40CFR35, Subpart B, Appendix A) outlines the minimum components of a state water quality monitoring program.

1. Compliance monitoring of permit dischargers.
2. Intensive surveys of surface waters.
3. Fixed station monitoring at representative points in surface waters.

Quality assurance procedures are required by the code and a list of references is provided which contain acceptable field and laboratory procedures. It is recommended that the states coordinate with other agencies collecting water quality data within the state and integrate such data into the state water quality program.

Fixed station/fixed frequency data records from the four states cooperating with this study; Colorado, Oregon, Illinois, and Maryland were surveyed. The purpose of the survey was to identify common sampling frequencies and to determine which water quality variables are commonly measured and have associated stream standards. A summary of the survey, as of November, 1980 is presented in Table 2.1.

It was found that most monitoring programs consist of sampling networks collecting about 12 grab samples per year. Grab samples are generally taken from a convenient access point to the river and are analyzed for variables which are regionally important. Often states collect data for variables for which they have no standard and do not collect data for a few variables for which standards have been designated. These discrepancies may be attributed to the ease with which some variables may be measured and the expense associated with others. Surprisingly, discharge is routinely monitored by only one state, Illinois. Since most states include in their standards document a flow exception policy, flow should be measured with other variables to determine when standards are in effect.

The U.S. Geological Survey collects some water quality information as a part of its water resources data collection operation. At selected locations, the U.S.G.S. collects water quality data similar to the information collected by state agencies, specifically, fixed station/fixed frequency quality analyses taken approximately monthly. The U.S.G.S. also collects a daily record of discharge, specific conductance, and water temperature at certain locations.

Synoptic surveys are conducted occasionally by state and federal data acquisition agencies. These surveys provide detailed information regarding specific locations but do not account for a large portion of the data available to a decision-maker. For this reason, the statistical procedures developed in upcoming chapters will be designed for fixed station/fixed frequency water quality data rather than synoptic survey data.

Table 2-1. A comparison of water quality variables for which stream standards have been established and for which data is collected in four selected states.[1]

Water Quality Variable	Colorado		Oregon		Illinois		Maryland	
	Std.[2]	Data	Std.	Data[3]	Std.	Data	Std.	Data
Flow						x		
Alkalinity		x			x			x
Aluminum	x	x						
Ammonia	x	x		x	x	x		x
Arsenic	x	x	x	x	x	x		
Barium	x		x	x	x	x		
Beryllium	x	x						
BOD		x		x				x
Boron	x	x	x	x	x			
Cadmium	x	x	x		x	x		x
Calcium		x						
Carbon dioxide (diss.)						x		
Chloride	x	x	x	x	x			
Chlorine	x						x	
Chlorophyll						x		x
Chromium	x	x	x	x	x	x		
Coliform, fecal	x	x	x		x	x	x	x
Coliform, total				x				x
COD								
TOC						x		
Conductivity		x		x		x		
Copper	x	x	x	x	x	x		
Cyanide	x	x	x	x	x			
Fluoride	x		x	x	x			
Gases, total dissolved			x					
Hardness		x		x				
Iron	x	x	x	x	x			x
Lead	x	x	x	x	x	x		x
Magnesium		x						
Manganese	x	x	x	x	x	x		
Mercury	x	x		x	x	x		
Molybdenum		x						

Table 2-1. (continued)

Water Quality Variable	Colorado		Oregon		Illinois		Maryland	
	Std.[2]	Data	Std.	Data[3]	Std.	Data	Std.	Data
Nickel	x	x			x			
Nitrogen, total Kjel.		x				x		x
Nitrogen, total					x			x
Nitrates	x	x		x				x
Nitrates & nitrites				x		x		
Nitrites	x	x						x
Oil and grease								
Oxygen, dissolved	x	x	x	x	x	x	x	x
pH	x	x	x	x	x	x	x	x
Phenol			x		x			x
Phosphorous		x		x	x	x		x
PO_4, total				x				
Potassium		x						
Residue, total nonfiltered				x				
Selenium	x	x			x	x		
Silica				x		x		x
Silver	x	x			x	x		
Sodium (Na, total)		x		x				
Sodium (absorption)		x						
Solids (suspended)		x				x		x
Solids (total dissolved)		x	x	x	x	x		
Sulfate	x	x		x	x	x		
Sulfide	x							
Temperature	x	x	x	x		x	x	
Thallium	x							
Turbidity	x	x	x	x		x	x	
Zinc	x	x	x		x			

Table 2-1. (continued)

Water Quality Variable	Colorado		Oregon		Illinois		Maryland	
	Std.[2]	Data	Std.	Data[3]	Std.	Data	Std.	Data
Pesticides, Herbicides, etc.								
Aldrin/Dieldrin	x						x	
Benzidine	x						x	
Chlordane								
Chlorophenol	x							
Chlorophenoxy herbicides								
DDT	x						x	
Demeton	x							
Endosulfan	x							
Endrin	x						x	
Guthion	x							
Heptachlor	x							
Lindane	x							
Malathion	x							
Methoxychlor	x							
Mirex	x							
Monohydric phenol	x							
Parathion	x							
Toxaphene	x						x	
PCB	x						x	
2,4-D	x							
Radioactive Materials			x					
Alpha		x						
Beta (gross)		x			x			
Cesium 134	x							
Cobalt						x		
Plutonium	x							
Radium	x				x			

Table 2-1. (continued)

Water Quality Variable	Colorado Std.[2]	Colorado Data	Oregon Std.	Oregon Data[3]	Illinois Std.	Illinois Data	Maryland Std.	Maryland Data
Strontium	x				x			
Thorium	x							
Tritium	x							
Uranium	x	x						

[1]The standards and monitoring data noted for water quality variables are general and do not reflect site-specific situations in the states.

[2]Standards vary depending upon classification. This is a list of criteria that may be standards depending upon river classification.

[3]Oregon's Department of Environmental Quality now measures some selected pesticides in fish tissue as part of EPA's Basic Water Monitoring Program. In Oregon, data on radioactive materials are collected by the Oregon State Health Division.

Chapter 3

PROCEDURES FOR THE ANALYSIS OF WATER QUALITY DATA

3.1 Introduction

This chapter will develop five analytical procedures for the assessment of river water quality. The procedures are designed for low frequency grab sample information and daily records of certain indicator variables such as flow and specific conductance. The five procedures consist of probability density function modeling, multiple linear regression modeling, conditional probability modeling of stream standard violations, an index indicating water quality changes, and an index of compliance/noncompliance of samples with stream standards. Each procedure provides information suitable for different situations, and the selection of which is most appropriate for a given application depends upon the availability of necessary data and management objectives.

Assessments of river quality obtained from the procedures relate to limiting-concentration type stream standards. The assessments include the determination of the daily probability of a stream standard violation, the expected number of stream standard violations in a period of time, the estimation of constituent concentration from indicator variables which are measured more often, and index values useful for the communcation of water quality conditions to nontechnical persons. The use of these assessments does not diminish the information content of individual samples, if an individual sample is found to be out of compliance with a stream standard, action may be taken based on that sample alone. Assessments provide information supplemental to the compliance/noncompliance of samples with standards.

In this work, reported measurements of all water quality variables including discharge, specific conductance, and chemical constituents are assumed to be representative of the entire day during which the sample was collected. With this assumption, assessments may be made regarding the daily behavior of water quality, such as the expected number of days per year a stream was in violation with standards. Without the assumption, no temporal meaning may be obtained from the conclusions drawn by the procedures. Conclusions drawn regarding individual samples (by not using the assumption) are rendered somewhat vague since the number of samples collected per year may vary widely.

The use of the assumption is generally appropriate for water quality analysis. Water quality variable concentration is usually highly correlated to discharge and, therefore, unless discharge has fluctuated appreciably on the day of the sample, it is reasonable to expect that a sample is fairly representative of conditions on the day it was collected. However, variables such as dissolved oxygen, which exhibit diurnal fluctuations, must be treated with care because the assumption is obviously less valid with these variables.

3.2 Application of Probability Distributions to Water Quality Variables

3.2.1 Background

3.2.1.1 Purpose

The purpose of this section is to develop criteria for the selection of probability density functions (probability distributions) in water quality analysis by fitting several probability distributions to real water quality data gathered by state agencies. A large number of density functions have been developed, and the selection of the most appropriate one for a given use is a fundamental task in the modeling procedure. The usefulness of modeling the behavior of a water quality variable with a probability distribution is that more understanding may be gained about the variable's movement (change in concentration with time) than by simply comparing individual samples with a standard. Five probability density functions were selected for analysis because of their common use in traditional hydrology. The normal, log-normal, gamma, Gumbel, and log-Gumbel distributions were fitted to several series of data and evaluated for applicability to water quality variables. A brief description of these density functions is presented in the next section, but the interested reader is urged to consult statistical references such as Benjamin and Cornell, 1970; Mood et al., 1974; Haan, 1977 for a more detailed discussion.

3.2.1.2 Probability Distribution Description

The normal distribution is the most widely used probability function in statistics. A random variable, say x, is normally distributed if its density is expressed as

$$f_x(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-(x_i - \mu)^2/2\sigma^2) \tag{3.1}$$

for $-\infty < x < \infty$

where x_i = random variable

μ = mean value of random variable

σ^2 = variance of random variable.

This distribution is symmetric about the mean value (skewness equal to zero) and is unbounded in both the positive and negative directions.

The mean and variance completely define the normal distribution, the mean as location parameter and the variance as scale parameter. Unbiased estimates of the mean and variance may be calculated from the sample series with Equations 3.2 and 3.3.

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \tag{3.2}$$

$$\hat{\sigma}^2 = \frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2 \tag{3.3}$$

where $\bar{x}$ = sample mean

$\hat{\sigma}^2$ = sample variance

N = number of samples.

Related to the normal distribution is the log-normal probability density function. If the logarithms of a random variable, say y, are normally distributed, the random variable is said to be log-normally distributed. The functional form of the distribution is identical to that of the normal distribution (Equation 3.1) with the substitution

$$x_i = \log_{10} y_i \text{ (1)} \tag{3.4}$$

Using the substitution of Equation 3.4, the unbiased estimates of the mean and variance may be determined as before (Equations 3.2 and 3.3). The log-normal distribution is positively skewed and is bounded at the left by zero, that is, $0 < y < \infty$.

The gamma distribution, the distribution of the sum of n exponentially distributed random variables, is defined as

$$f_x(x) = \frac{\lambda(\lambda x_i)^{n-1} \exp(-\lambda x_i)}{(n-1)!} \tag{3.5}$$

---

(1) Either the base 10 or natural logarithm may be used.

for $\quad x \geq 0$

where $\quad n = 1, 2, 3, \ldots$

λ = a distribution parameter.

If n is not an integer the gamma distribution is defined

$$f_x(x) = \frac{\lambda(\lambda x_i)^{\eta-1} \exp(-\eta x_i)}{\Gamma(\eta)} \tag{3.6}$$

where $\quad \Gamma(\eta) = \int_0^\infty t^{\eta-1} \exp(-t)\, dt$

The mean and variance for the discrete case are

$$\mu = \frac{n}{\lambda} \tag{3.7a}$$

$$\sigma^2 = \frac{n}{\lambda^2} \tag{3.8a}$$

and for the continuous case

$$\mu = \frac{\eta}{\lambda} \tag{3.7b}$$

$$\sigma^2 = \frac{\eta}{\lambda^2} \tag{3.8b}$$

A notable feature of the gamma distribution is the variety of shapes it may take depending upon the parameters of the distribution, n and λ. When $n=1$ the gamma distribution reduces to the exponential distribution with parameter λ. For other combinations of n and λ the gamma may resemble the log-normal distribution, bounded at the left by zero and positively skewed; or it may be nearly symmetric about the mean and bounded at the left by zero. From Equations 3.7b and 3.8b the moment estimates of the parameters of the gamma distribution may be determined.

$$\hat{\lambda} = \frac{\bar{x}}{\hat{\sigma}^2} \tag{3.9}$$

$$\hat{\eta} = \frac{\bar{x}^2}{\hat{\sigma}^2} \qquad (3.10)$$

The Gumbel distribution, also known as the extreme value distribution and the double exponential distribution, is defined

$$f_x(x) = \frac{\exp[\pm w_i - \exp(\pm w)]}{\alpha} \qquad (3.11)$$

for $-\infty < x < \infty$; $-\infty < \beta < \infty$; $\alpha > 0$

where $$w_i = \frac{x_i - \beta}{\alpha} \qquad (3.12)$$

α = a distribution parameter

β = a distribution parameter.

It is typically used for extreme value statistics with the negative signs associated with maximum values (such as floods) and the positive signs associated with minimum values (such as low flows). The mean and variance of the Gumbel distribution are

$$\mu = \beta + 0.577\ \alpha \text{ (maximum)} \qquad (3.13)$$

$$= \beta - 0.577\ \alpha \text{ (minimum)} \qquad (3.14)$$

$$\sigma^2 = 1.645\ \alpha^2 \quad \text{(both)} \qquad (3.15)$$

The coefficient of skewness is a constant 1.1396 for the Gumbel distribution and the moment estimators are

$$\hat{\alpha} = \frac{\hat{\sigma}}{1.283} \qquad (3.16)$$

$$\hat{\beta} = \bar{x} - 0.45\ \hat{\sigma} \text{ (maximum)} \qquad (3.17)$$

$$= \bar{x} + 0.45\ \hat{\sigma} \text{ (minimum)} \qquad (3.18)$$

If the logarithms of a random variable, say y, are Gumbel distributed, the random variable is said to be log-Gumbel distributed and Equations 3.11-3.18 are applicable with the transformation

$$x_i = \log_{10} y_i \quad . \tag{3.4}$$

The log-Gumbel distribution is bounded on the left by zero, $0 < y < \infty$, and may be expected to fit highly skewed data.

3.2.1.3 Data Used in Analysis

State water quality data obtained from STORET were used in this analysis. Eight stations, two in Colorado and six in Illinois were selected and data records from each were reviewed. Dissolved oxygen and specific conductance records were found to be fairly complete over the period of data collection (approximately 10 years) for all the stations so these variables were selected for the study. The data records consisted of samples taken at various sampling frequencies throughout the period of record but the most common frequency was approximately one sample per month.

The process of fitting probability density functions to these sets of data required three conditions to be achieved; consistency of sample collection and analysis, temporal stationarity of the variables, and temporal independence of the samples. It was assumed that over the period of record samples were collected from exactly the same location and by the same procedures and that laboratory procedures were consistent because different analytical methods may yield slightly differing results. Inherent in the use of probability density functions is the requirement of process stationarity. If trending exists in the data it must be removed by appropriate statistical techniques before a distribution may be fitted to the data. To check for stationarity, annual means were calculated for both variables and plotted against time for each station. Regression equations were determined and found to have slopes not significantly different than zero indicating temporal stationarity (Sanders, 1974). Finally, the requirement of temporal independence of the samples was reviewed. Research conducted by Loftis (1978) on daily records of water quality variables indicated relatively high serial correlations for short lags. The serial correlations generally dropped to very low values after about lag 20, however, suggesting temporal independence of samples collected at least three weeks apart. The water quality data used in this study, in general, had sampling frequencies significantly longer than three weeks supporting the condition of temporal independece of samples.

3.2.2 Methodology

3.2.2.1 Model Parameter Estimation

The parameters of the normal, log-normal, gamma, Gumbel, and log-Gumbel distributions were estimated for each data set using computer programs developed at Colorado State University (Salas, 1978). These programs utilized the method of maximum likelihood for parameter estimation. This procedure maximizes the likelihood function or for some distributions, the log-likelihood function for each distribution to determine optimal distribution parameters for a given data set.

3.2.2.2 "Goodness of Fit" Criteria

The "goodness of fit" of each distribution was compared to the fit of others with a chi-square test. For a given or hypothesized probability distribution, this test computes the expected number of occurrences of a random variable in a specified class interval. The number of observed occurrences in the class interval is subtracted from the expected number in the same class interval. This difference is squared and divided by the expected number. These normalized, squared differences are summed over the entire range of possible values of the random variable and the sum may be considered a measure of "goodness of fit".

$$\chi^2 = \sum_{i=1}^{N} \frac{(O_i - E_i)^2}{E_i} \qquad (3.19)$$

where χ^2 = chi-square statistic

N = number of class intervals

O_i = number of observed occurrences

E_i = expected number of occurrences.

The chi-square statistic is usually compared to a critical value obtained from a table to determine if the distribution fits at a specified level of significance. In this study, however, the computed chi-square values were used primarily to compare one distribution to another. This work is similar to that of Sherwani and Moreau (1975) who have used the chi-square test to compare the fit of various distributions in their work at the University of North Carolina. The number of class intervals used in the chi-square test should be selected by the user such that a minimum of five points is expected to fall within each interval (Benjamin and Cornell, 1970). In this study, class intervals numbering six, seven, and eight were utilized.

3.2.3 Results

The five probability density functions used in this study were fitted to each data series. Chi-square "goodness of fit" statistics are shown in Table 3-1. A tabular summary indicating data sets "best fit" and "significantly fit" by the probability functions is shown in Table 3-2.

Often the shape of a distribution is well indicated by data skewness, therefore, a criteria for the selection of a probability distribution to model water quality data based upon the sample coefficient of skew will be presented. The sample coefficient of skew, $\hat{g}$, may be determined by Equation 3.20.

$$\hat{g} = \frac{N \sum_{i=1}^{N} (x_i - \bar{x})^3}{(N-1)(N-2)(\hat{\sigma}^2)^{3/2}} \tag{3.20}$$

where x_i = random variable

$\bar{x}$ = sample mean (Equation (3.2))

$\hat{\sigma}^2$ = sample variance (Equation (3.3))

N = number of data points.

From Table 3-2 it can be seen that none of the probability distributions fit at the selected level of significance (5 percent) when the sample coefficient of skew was greater than about 2.0 or less than about -1.0. For values of $\hat{g}$ between these limits, the normal, log-normal, and gamma distributions fit at the selected significance level more frequently than the Gumbel or log-Gumbel distributions. The normal and gamma distributions were most often the best fitting models, i.e., the model with the lowest chi-square statistic, within this range of skewness. The Gumbel distribution, with constant skew of 1.1396, appears to be the best fitting model for data sets with positive skew coefficients in the range of 1.0 to 2.0. Data sets with the highest positive coefficients of skew of the sets used in this study were best fit by the Gumbel rather than the distribution expected to fit well in this range, the log-Gumbel distribution.

Table 3-1a. Chi-square statistics indicating how well various probability distributions fit the data sets using six class intervals.

River Location	Dissolved Oxygen Normal Dist.	Dissolved Oxygen Log-Normal Dist.	Dissolved Oxygen Gamma Dist.	Dissolved Oxygen Gumbel Dist.	Dissolved Oxygen Log-Gumbel Dist.	Conductivity Normal Dist.	Conductivity Log-Normal Dist.	Conductivity Gamma Dist.	Conductivity Gumbel Dist.	Conductivity Log-Gumbel Dist.
Cache La Poudre near Greeley, CO	4.72*	11.03	5.98*	12.48	19.86	26.52	77.74	64.70	102.78	222.35
South Platte at Henderson, CO	23.23	6.06*	8.10*	5.05*	6.97*	56.24	91.62	51.24	52.17	--
Little Wabash at Louisville, IL	7.39*	16.94	10.79	15.88	54.06	1.78*	9.33*	3.56*	4.22*	25.33
Chicago Ship Canal at Lockport, IL	98.27	5.82*	2.73*	14.55	12.55	6.98*	6.65*	8.28*	5.67*	12.51
Vermillion at Pontiac, IL	5.19*	3.06*	2.86*	1.89*	19.78	10.04	20.27	19.00	27.59	67.68
Illinois at Ottawa, IL	7.00*	10.25	6.75*	8.75*	29.75	8.55*	6.77*	6.77*	13.91	16.30
Kankakee at Will City Line, IL	4.83*	10.00	10.00	13.96	23.39	24.84	27.02	27.02	36.04	52.22
Sangamon at Decatur, IL	11.02	6.15*	7.07*	5.54*	39.78	4.93*	8.36*	7.42*	23.91	33.24

*Chi-square static less than critical value, $\chi^2_{.05,4} = 9.49$.

Table 3-1b. Chi-square statistics indicating how well various probability distributions fit the data sets using seven class intervals.

River Location	Dissolved Oxygen: Normal Dist.	Log-Normal Dist.	Gamma Dist.	Gumbel Dist.	Log-Gumbel Dist.	Conductivity: Normal Dist.	Log-Normal Dist.	Gamma Dist.	Gumbel Dist.	Log-Gumbel Dist.
Cache La Poudre near Greeley, CO	12.89	7.27*	6.98*	11.59	27.02	23.10	87.89	58.18	106.78	245.61
South Platte at Henderson, CO	31.74	7.61*	15.10	6.06*	8.65*	64.77	91.63	49.35	46.93	--
Little Wabash at Louisville, IL	10.85*	16.91	8.67*	21.76	68.55	3.16*	4.94*	4.43*	6.71*	28.56
Chicago Ship Canal at Lockport, IL	73.53	3.51*	16.39	37.69	10.99*	6.30*	6.67*	10.02*	6.67*	8.53*
Vermillion at Pontiac, IL	4.44*	7.33*	4.22*	12.44	29.56	14.91	25.09	19.27	49.09	72.73
Illinois at Ottawa, IL	11.43	10.00*	8.00*	10.00*	21.71	12.06	15.47	12.40	16.49	15.81
Kankakee at Will City Line, IL	11.04*	8.26*	8.26*	12.43	20.78	21.67	41.93	39.09	45.49	45.49
Sangamon at Decatur, IL	11.65	6.78*	6.43*	6.78*	20.39	4.96*	5.67*	5.67*	19.53	29.13

*Chi-square statistic less than critical value, $\chi^2_{.05,5} = 11.1$.

Table 3-1c. Chi-square statistics indicating how well various probability distributions fit the data sets using eight class intervals.

River Location	Dissolved Oxygen: Normal Dist.	Dissolved Oxygen: Log-Normal Dist.	Dissolved Oxygen: Gamma Dist.	Dissolved Oxygen: Gumbel Dist.	Dissolved Oxygen: Log-Gumbel Dist.	Conductivity: Normal Dist.	Conductivity: Log-Normal Dist.	Conductivity: Gamma Dist.	Conductivity: Gumbel Dist.	Conductivity: Log-Gumbel Dist.
Cache La Poudre near Greeley, CO	13.62	13.78	9.24*	16.38	20.43	30.12	85.47	63.11	117.66	250.71
South Platte at Henderson, CO	26.39	13.18	17.24	9.55*	12.16*	67.20	112.58	57.49	54.65	--
Little Wabash at Louisville, IL	10.09*	22.64	10.09*	22.09	58.09	4.00*	5.14*	3.71*	5.14*	31.14
Chicago Ship Canal at Lockport, IL	90.75	6.25*	22.14	53.35	15.83	6.60*	5.77*	2.42*	4.51*	17.91
Vermillion at Pontiac, IL	12.00*	9.50*	7.50*	17.25	25.50	17.55	30.45	31.27	37.00	27.49
Illinois at Ottawa, IL	10.21*	13.11	10.86*	13.11	24.04	16.77	19.83	19.06	23.66	27.49
Kankakee at Will City Line, IL	10.35*	14.26	13.48	20.91	17.39	25.20	31.60	33.20	60.00	76.80
Sangamon at Decatur, IL	10.13*	9.35*	7.78*	15.80	25.59	3.20*	16.00	12.80	20.40	46.80

*Chi-square statistic less than critical value, $\chi^2_{.05,6} = 12.6$.

Table 3-2. Summary of sample coefficients of skew and probability distribution fit information for data sets used in the study.

River	Variable	Sample Coefficient of Skew	Number of Significant Fits (1): Normal	log-Normal	Gamma	Gumbel	log-Gumbel	Number of Best Fits (2): Normal	log-Normal	Gamma	Gumbel	log-Gumbel
Vermillion	Conductivity	-1.704	0	0	0	0	0	3	0	0	0	0
Cache La Poudre	Conductivity	-1.541	0	0	0	0	0	3	0	0	0	0
Kankakee	Conductivity	-1.240	0	0	0	0	0	3	0	0	0	0
Sangamon	Conductivity	-.735	3	2	2	0	0	3	0	0	0	0
Little Wabash	D.O.	-.231	3	0	2	0	0	1½ (3)	0	1½ (3)	0	0
Vermillion	D.O.	-.021	3	3	3	1	0	0	0	2	1	0
Sangamon	D.O.	.004	1	3	3	2	0	0	0	2	1	0
Illinois	D.O.	.057	2	1	3	2	0	1	0	2	0	0
Cache La Poudre	D.O.	.060	1	1	3	0	0	1	0	2	0	0
Little Wabash	Conductivity	.200	3	3	3	3	0	1	0	2	0	0
Illinois	Conductivity	.231	1	1	1	0	0	2	½ (3)	½ (3)	0	0
Kankakee	D.O.	.454	3	1	1	0	0	2	½ (3)	½ (3)	0	0
Chicago Ship Canal	Conductivity	1.184	3	3	3	3	1	1	0	1	1	0
South Platte	D.O.	1.832	0	2	1	3	3	0	0	0	3	0
Chicago Ship Canal	D.O.	1.918	0	3	1	0	1	0	2	1	0	0
South Platte	Conductivity	6.514	0	0	0	0	0	0	0	1	2	0

(1) The chi-square statistic was calculated for 6, 7, and 8 class intervals, the number of significant fits indicates how many times, out of 3, the distribution fit at the 10% significance level.
(2) Number of times out of 3 that the distribution had smallest chi-square statistic.
(3) Two models fit equally well.

Water quality data sets with negative coefficients of skew are not uncommon. Many variables are inversely proportional to flow, which is often positively skewed making the distribution of the variable negatively skewed. In this study, the normal distribution was the best fitting model for data sets with negative coefficients of skew even though the skewness of the normal distribution is zero. This may be explained by the fact that all of the other distributions used in this study are positively skewed so consequently they fit these data sets less well than the normal distribution. It should also be noted that even though the normal distribution was the best fitting model for negatively skewed data sets, it did not fit at the significance level for data sets with skewness coefficients more negative than -0.735.

The gamma distribution appears to be the most flexible distribution in terms of fitting data sets of differing coefficients of skew. This result may be explained by the large number of shapes this distribution may take on, depending upon the values of its parameters. The gamma distribution commonly fit significantly well, the data sets with a range of skew from -0.735 to 1.918. It was most often the best fitting model over the same range and often fit slightly better than the log-normal distribution when the log-normal fit relatively well. This result suggests the gamma distribution may be most appropriate for the data sets that are commonly modeled with the log-normal distribution, i.e., data sets with moderately positive skewness.

Table 3-3 presents a simple criteria for the selection of a probability distribution to model water quality variables (of those used in this study) based on sample coefficient of skew.

Table 3-3. Criteria for probability model selection.

Sample Coefficient of Skew	Recommended Probability Model
< -1.0	None
-1.0 - 0.1	Normal
0.1 - 1.0	Gamma
1.0 - 2.0	Gumbel
2.0 <	None

3.2.4 Discussion

3.2.4.1 Applications

This section will present possible uses of probability distributions in water quality management. The methods described in the following paragraphs will be illustrated in further detail in the case study presented in Chapter 4.

The most obvious use of probability modeling in water quality management is the assessment of the daily probability of a water quality variable being in violation of a standard. The violation probability may be determined by integrating the selected probability density function over values of the variable from the standard to infinity in the case of a maximum-limit standard (Eq. 3.21a) and from minus infinity to the standard in the case of a minimum-limit standard (Eq. 3.21b).

$$P[V] = \int_{s}^{\infty} f_x(x)\, dx \tag{3.21a}$$

$$P[V] = \int_{-\infty}^{s} f_x(x)\, dx \tag{3.21b}$$

where $P[V]$ = daily probability of stream standard violation for variable x

s = stream standard for variable x

$f_x(x)$ = probability density function of variable x.

A stream standard expressed as a limiting concentration not to be exceeded by an average daily probability greater than a specified value could be directly enforced with routine water quality data. A similar approach would be a standard expressed as a limiting concentration not to be exceeded on more than a specified number of days per year. An estimate of the expected number of days per year the variable is in violation of the standard may be obtained by multiplying the daily violation probability by 365.

$$E[V] = P[V] \times 365 \qquad (3.22)$$

where $E[V]$ = expected number of violations in one year.

These approaches do not take into account the effects of high or low runoff or changes in the water quality system due to man-made or natural alterations but do provide a simple approach by which water quality may be assessed with respect to limiting-concentration type stream standards.

A more detailed approach which does incorporate the effect of discharge is the development of probability models conditioned on high or low flows. With sufficient records, data may be partitioned into subsets of known conditions such as above average and below average discharge and probability distributions may be fitted to each subset. For this case, the expected number of days, in a given year, a variable is in violation with the standard may be determined as follows.

$$E[V] = P[V_A] \times N + P[V_B] \times N' \qquad (3.23)$$

where $P[V_A]$ = daily probability of stream standard violation for variable x on days with high flow

$P[V_B]$ = daily probability of stream standard violation for variable x on days with low flow

N = number of days in a particular year with above average flow

N' = number of days in a particular year with below average flow.

This technique may also be used by conditioning on variables other than flow, for example, specific conductance (if a daily record of conductivity is available).

The detection of a change in the water quality system is often a difficult task. Probability modeling may provide a means for the detection of such changes. The probability of collecting a sample with a certain concentration or a group of n samples with associated concentrations may be determined from either the lumped distribution or a set of partitioned data distributions.

$$P[Y] = P[C_i]^n \tag{3.24}$$

where $P[Y]$ = probability of collecting n consecutive random samples above a specified concentration.

$P[C_i]$ = daily violation probability associated with the specified concentration (C_i)

n = number of samples

C_i = a specified concentration.

For example, the probability, $P[Y]$, of getting three consecutive random samples greater than one standard deviation above the mean from a normal distribution may be determined.

$$P[C_i] = 0.1587$$

$$n = 3$$

$$P[Y] = (0.1587)^3$$

$$= .0040 \quad \text{or about 1 time in 250.}$$

It can be seen that the occurrence of three samples having concentration greater than the mean plus one standard deviation is very unlikely and perhaps a change in the system has caused these high concentrations.

Another approach to detecting changes in water quality variable behavior and determining more precisely the violation probability for a given year is the fitting of probability distributions to annual data. Routine monitoring stations typically collect data on a monthly basis resulting in only 12 samples per year. The techniques described in preceeding paragraphs are applicable to such yearly data, but the accuracy of sample statistics calculated from small annual samples is obviously poorer than from larger samples (an analysis of the expected accuracy of annual statistical parameters based on various sampling frequencies is included in Appendix B). Since probability distribution parameters are often determined from sample statistics, less confidence may be placed in annual distributions than in distributions determined from larger samples. However, changes in water quality may be estimated by statistically determining if different annual sample series come from the same population.

An argument against the use of probability distributions in water quality management has been that many of the analyses may not be performed until a relatively large number of samples have been collected. By the time sufficient samples are collected, perhaps a year or several years, statistical conclusions drawn from the data describe "past history" and thus may not be used to enforce stream standards.

It has been widely recognized, however, that stream standards cannot practicably be enforced by stream monitoring anyway. For this reason, emphasis of compliance monitoring has been changed from stream standards to effluent discharge permits. The use of probability modeling may not aid in directly enforcing limiting-concentration type stream standards but will provide a rational method by which general river water quality may be assessed. A method to evaluate violation probabilities on a more timely basis will be presented in following sections.

3.2.4.2 Summary

Based on the limited results of this study, it appears that three distributions, the normal, gamma, and Gumbel may adequately model water quality data with sample coefficients of skew in the range of -1.0 to 2.0. More research is needed, however, to substantiate this finding and to determine probability distributions which model negatively skewed data more accurately. The normal distribution may be expected to fit data sets acceptably well for values of skewness moderately negative and near zero, the gamma distribution for values of skewness moderately positive, and the Gumbel distribution for values of skewness highly positive.

3.3 Regression Analysis of Water Quality Variables

3.3.1 Background

This section presents the use of multiple linear regression modeling in water quality management. The use of this type of modeling allows the estimation of water quality variable concentration from known conditions such as discharge, specific conductance, and water temperature. These estimates may be made daily, provided daily measurements of indicator variables are made, and give management agencies information regarding the likely concentration of important variables on days when no direct samples are collected. This information may be used to enhance an agency's ability to evaluate and manage river water quality.

Effective multiple regression modeling requires strong cross-correlation between indicator variables and the unknown variables of interest. Researchers in water quality hydrology have shown concentrations of inorganic constituents often change with associated changes in stream discharge and specific conductance. Studies by Lane (1975), Sherwani and Moreau (1975), Durum (1953), and others have shown that concentrations of inorganic variables are inversely proportional to streamflow. This relationship occurs because of dilution of highly mineralized ground water flow by surface runoff during periods of high flows. Other research, Gunnerson (1967), Ledbetter and Gloyna (1964), has shown estimates of concentrations of major ions may be obtained from total dissolved solids concentrations or by specific conductance measurements. Temperature, while not as important as an indicator of ion concentration as discharge and specific conductance, probably relates to ion concentration somewhat because of higher soluability of inorganics in warmer water.

The U.S. Geologic Survey collects a daily record of flow, conductivity, and temperature at selected stream sites as a part of its routine monitoring of surface waters. At some locations complete water quality analyses similar to those collected by state agencies are performed approximately once a month. Data collected at two such locations in the western United States, the Henrys Fork near Linwood, Utah, and the Gunnison River near Grand Junction, Colorado, were used to develop multiple linear regression models to estimate various ion concentrations at these sites.

3.3.2 Methodology

The Biomedical Computer Programs, BMD02R, Stepwise Regression program available on the Colorado State University computer system was used in the regressions. The multiple linear regression model may be expressed as follows

$$\hat{Y} = \sum_{i=1}^{n} \beta_i \; x_i + \beta_{n+1} \tag{3.25}$$

where $\hat{Y}$ is the dependent variable, x_i are independent variables, β_i are regression coefficients determined by minimizing the sum of squared errors, and n is the number of independent variables. The BMD program uses a stepwise procedure in which the most important independent variable is initially included and the lesser important variables are added to the regression sequentially. Importance of independent variables is determined by comparison of the correlation coefficient of each independent variable taken separately with the dependent variable. Regressions were performed using three independent variables and the following transformations

$$\hat{Y} = \beta_1 \; x_1 + \beta_2 \; x_2 + \beta_3 \; x_3 + \beta_4 \tag{3.26}$$

$$\hat{Y} = \beta_1 \; \ell n x_1 + \beta_2 \; \ell n x_2 + \beta_3 \; \ell n x_3 + \beta_4 \tag{3.27}$$

$$\ell n \; \hat{Y} = \beta_1 \; x_1 + \beta_2 \; x_2 + \beta_3 \; x_3 + \beta_4 \tag{3.28}$$

$$\ell n \; \hat{Y} = \beta_1 \; \ell n x_1 + \beta_2 \; \ell n x_2 + v_3 \; \ell n x_3 + \beta_4 \tag{3.29}$$

where $\hat{Y}$ = an estimate of water quality variable Y

x_1 = discharge in cfs

x_2 = specific conductance in μmhos/cm at 25°C

x_3 = temperature in °F or °C

The squared correlation coefficients, r^2, were calculated for each variable and transformation and are presented in the regression summaries (Table 3-4).

3.3.3 Results

The water quality variables boron and sulfate at the Henrys Fork location were found to fit the multiple linear regression model quite well with correlation coefficients of 0.9169 and 0.9310 respectively. Simulated records of these variables based on historical records of flow, conductivity, and temperature for the water year 1971 are shown in Figures 3-1 and 3-2. These simulated time series represent average responses of boron and sulfate and may not accurately indicate extreme events resulting from spills, very low flows, floods, etc. The data used in the model calibration, however, incorporated a large range of flows and water quality concentrations and should accurately predict concentrations within the range used in the calibration. No particular form of the model, i.e., log-log, log-linear, linear-log, or linear-linear, seemed to fit consistently better than any other form but the BMD program is relatively inexpensive to run so analysis of all possibilities is not an expensive procedure. Of the three independent variables, flow was generally the most important followed by conductivity and temperature.

3.3.4 Discussion

3.3.4.1 Applications

Multivariate regression modeling may be used to provide information when samples are not directly taken. This information may

Table 3-4. Summary of correlation coefficients, r^2, obtained with the multiple linear regression model.

Henrys Fork near Linwood, Utah

Dependent-Independent Variable Variable	Fe	NO_3	B	pH	Na	HCO_3	SO_4
Linear-Linear	.0758	.5032	.9169	.2746	.8145	.4375	.9056
Linear-Ln	x	x	.8447	x	.8673	.4340	.8878
Ln-Linear	x	x	.8969	x	.8344	.5597	.9310
Ln-Ln	x	x	.8506	x	.8790	.5582	.9254

Gunnison River near Grand Junction, Colorado

Dependent-Independent Variable Variable	SiO_2	Na	K	HCO_3	PO_4	Ca+Mg	SO_4	B	Cl	Fl	NO_3	TDS
Linear-Linear	.2341	.9751	.3871	.9649	.7701	.9547	.9945	.2667	.7497	.7920	.8380	.4818
Linear-Log	.2389	.9731	.4126	.9716	.6611	.9306	.9673	.2859	.7782	.7270	.7093	.3867
Ln-Linear	.1991	.9875	.5144	.9730	.4871	.9682	.9930	.2431	.8582	.6860	.7747	.3127
Ln-Ln	.2198	.9828	.5298	.9783	.3563	.9685	.9978	.3209	.8974	.6690	.7060	.1911

x - model not calculated.

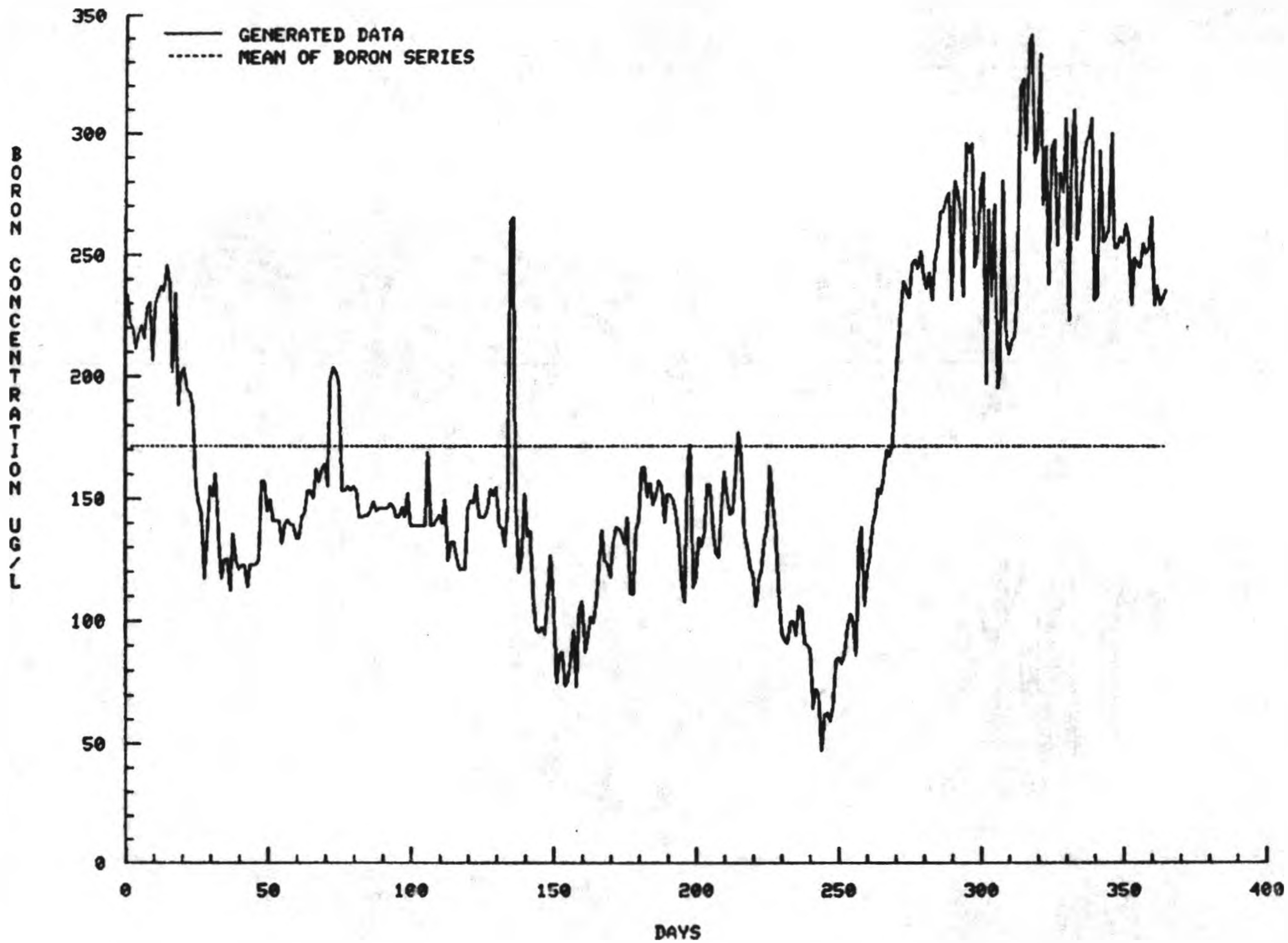

Figure 3-1. Multiple linear regression generation of boron concentration for Henry's Fork River near Linwood, Utah, water year 1971.

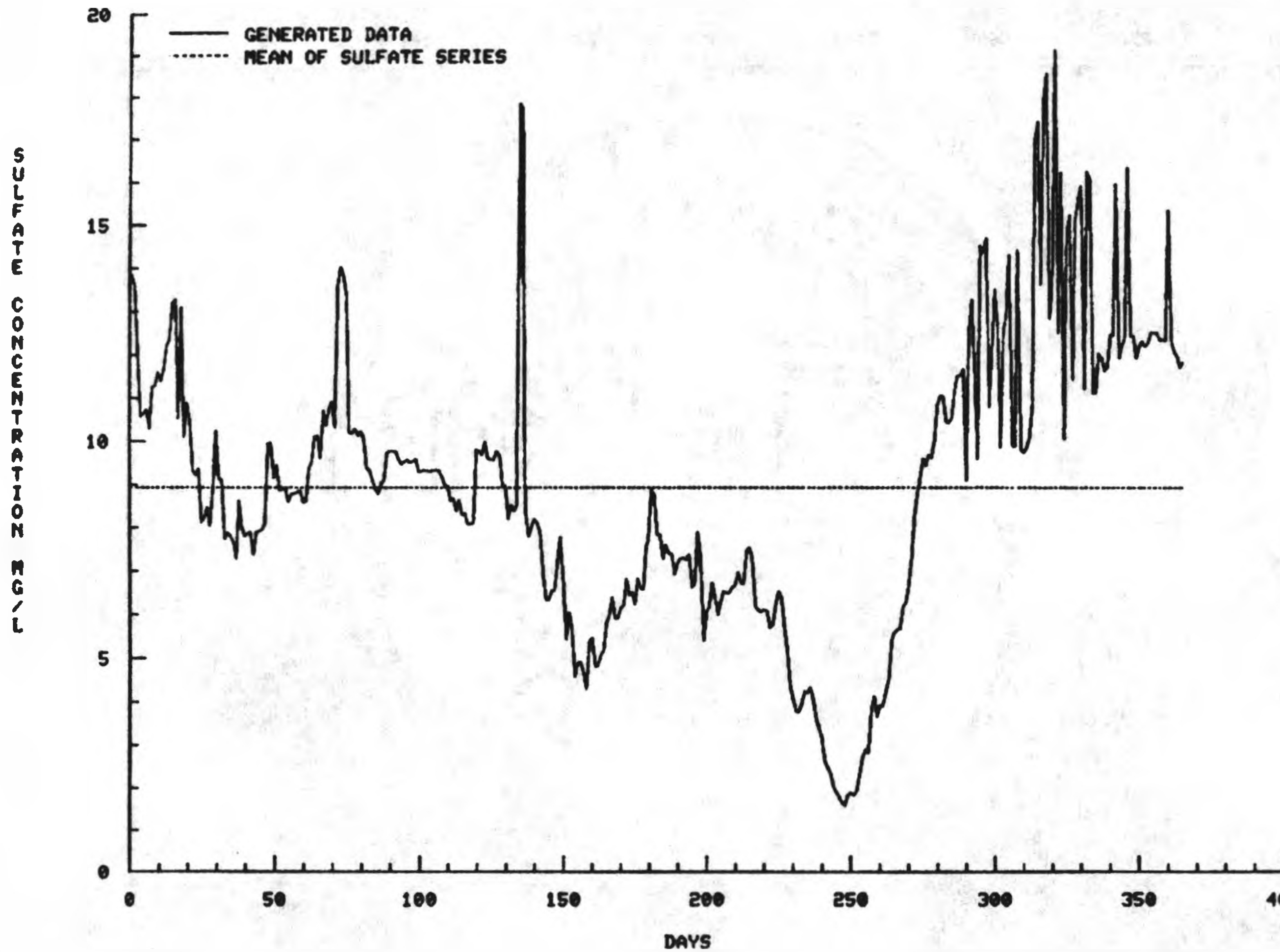

Figure 3-2. Multiple linear regression generation of sulfate concentration for Henry's Fork River near Linwood, Utah, water year 1971.

then be used to indicate periods of time when samples should be collected. Also, if strong correlations are found, the number of samples collected per year and/or the number of variables analyzed may be reduced. Determination of seasonal and annual mean concentrations may be made by averaging daily model estimates and may provide more accuracy than the averaging of relatively small samples. In general, however, the annual variance should not be calculated from regression estimates. Other information available from regression modeling includes estimation of the magnitude and duration of violation events.

3.3.4.2 Summary

The usefulness of regression modeling involves the utilization of more available information than an individual water quality sample. At stream sites where daily flow, conductivity and temperature data and periodic comprehensive surveys are made, daily time series of water quality variables may be generated. These time series allow further assessment of the range of magnitude, percentage of time in violation, and duration of water quality violations. The usefulness of the model is contingent, of course, on obtaining an acceptable fit with historic data. The regression parameters fitted to historic data should, when possible, be recalculated periodically utilizing subsequent monitoring information to keep the model current with respect to ion concentration as a function of the independent variables.

3.4 Conditional Probability Distributions of Water Quality Variables

3.4.1 Background

3.4.1.1 General Comments

The use of conditional probability distributions in water quality management was suggested in Section 3.2.4.1. This section will propose a more detailed methodology for the determination of conditional probability distributions for water quality variables. In the preceeding discussion, the partitioning of data into groups associated with another variable, one with a more complete record, was introduced to gain a better understanding of a variable's range of concentration over a period of time. The procedure developed in this section will perform the same function by combining the regression technique of Section 3.3 and the lumped data distribution technique described in Section 3.2. Data used in this analysis are the same records as used in the regression discussion.

3.4.1.2 Model Derivation

Cross correlations between water quality variables are the basis for the development of multivariate regression models. These cross correlations, however, do not explain the total variance of water quality variables as evidenced by correlation coefficients less than unity found in Section 3.3. Part of a variable's total variance may be attributed to random behavior not linked to other variables through cross correlation. The lower the total correlation coefficient, the greater the proportion of total variance not explained by the regression model. The deterministic variance component, the variance of the regression model, is necessarily less than the total variance. To incorporate the total variance into the multiple linear regression model, a random component, ε, must be added to Equation 3.25.

$$Y = \sum_{i=1}^{n} \beta_i x_i + \beta_{n+1} + \varepsilon \tag{3.30}$$

Y = observed value of a water quality variable where ε = an independent noise term.

This expression may be combined with Equation 3.25

$$Y = \hat{Y} + \varepsilon \tag{3.31}$$

and with

$$Z = Y - \hat{Y} \tag{3.32}$$

to obtain

$$Z = \varepsilon \quad . \tag{3.33}$$

The expected value of the residual series, Z, is zero due to the parameter estimation procedure used in the calibration of the multiple regression model. The variance of Z is generally not equal to zero and is expressed, σ_Z^2. By Equation 3.33 is can be seen that ε has mean zero and variance equal to σ_Z^2. If the residual series is assumed to follow the normal distribution, ε may now be expressed

$$\varepsilon = \sigma_Z \, \xi \tag{3.34}$$

where ξ = white noise term N(0,1)

and Equation 3.30 may be rewritten

$$Y = \sum_{i=1}^{n} \beta_i \, x_i + \beta_{n+1} + \sigma_z \, \xi \quad . \tag{3.35}$$

The variance of a sum of random variables, say V = W + Z, may be determined by

$$\text{VAR[V]} = \text{VAR[W]} + \text{VAR[Z]} - 2 \ \text{COV[WZ]} \tag{3.36}$$

where VAR = variance

COV = covariance.

Therefore, since $\hat{Y}$ and ε are independnet, their covariance is equal to zero, and the total variance of Y is equal to the sum of the variance of the deterministic component, $\hat{Y}$, and the random component σ_Z^2.

3.4.2 Methodology

The probability of a stream standard violation given values of discharge, conductivity, and water temperature may be directly assessed with knowledge of the residual variance. Combining Equations 3.33 and 3.34 yields

$$Z = \sigma_Z \xi \quad . \tag{3.37}$$

Now, define the magnitude of the residual, z, as

$$z = S - \hat{Y} \tag{3.38}$$

where z = magnitude of residual

S = stream standard concentration

$\hat{Y}$ = regression estimate of Y concentration.

By rearranging Equation 3.37 it can be seen that a residual, Z, of magnitude z, requires a white noise term of

$$\xi = \frac{z}{\sigma_Z} \tag{3.39}$$

The probability of obtaining a white noise term at least this large may be found in a cumulative standard normal table. This probability is the conditional probability of a stream standard violation given values of discharge, conductivity, and water temperature. If the covariances between the dependent variable and the independent variables are zero, it can be seen the model of Equation 3.35 reduces to an unconditioned normal distribution.

The assumption of residual series normality is not a requirement of the procedure. Other distributions which allow the random variable to take on both positive and negative values may be used providing the cumulative probability of the critical standard deviate may be evaluated. The normal distribution was used in this work because of the ease of using cumulative standard normal deviate tables and because the normal distribution fit the residual series quite well. The "goodness of fit" of this model may be determined by testing the residual series for normality and independence with the other variables.

3.4.3 Results

The probabilities of stream standard violations conditioned on historic discharge, conductivity, and temperature records for the water year 1971 for the Henrys Fork River near Linwood, Utah are shown in Figures 3-3 and 3-4. A further illustration of this procedure is included in Chapter 4.

3.4.4 Discussion

3.4.4.1 Applications

Possible uses of conditional probabilities in water quality management include all of the possible uses of unconditioned probability models suggested in Section 3.2. The probability of a stream standard violation may be estimated on a daily basis and contribute timely information assisting in the decision of when sampling should be undertaken. The expected number of days per year or month in violation may be obtained by summing the conditional probabilities for each day.

$$E[V] = \sum_{i=1}^{N} P[V|x_1, x_2, x_3] \tag{3.40}$$

where $E[V]$ = expected number of days in violation of stream standard

$P[V|x_1, x_2, x_3]$ = conditional probability of violation of stream standard, given discharge, conductivity, and temperature.

N = number of days in interval.

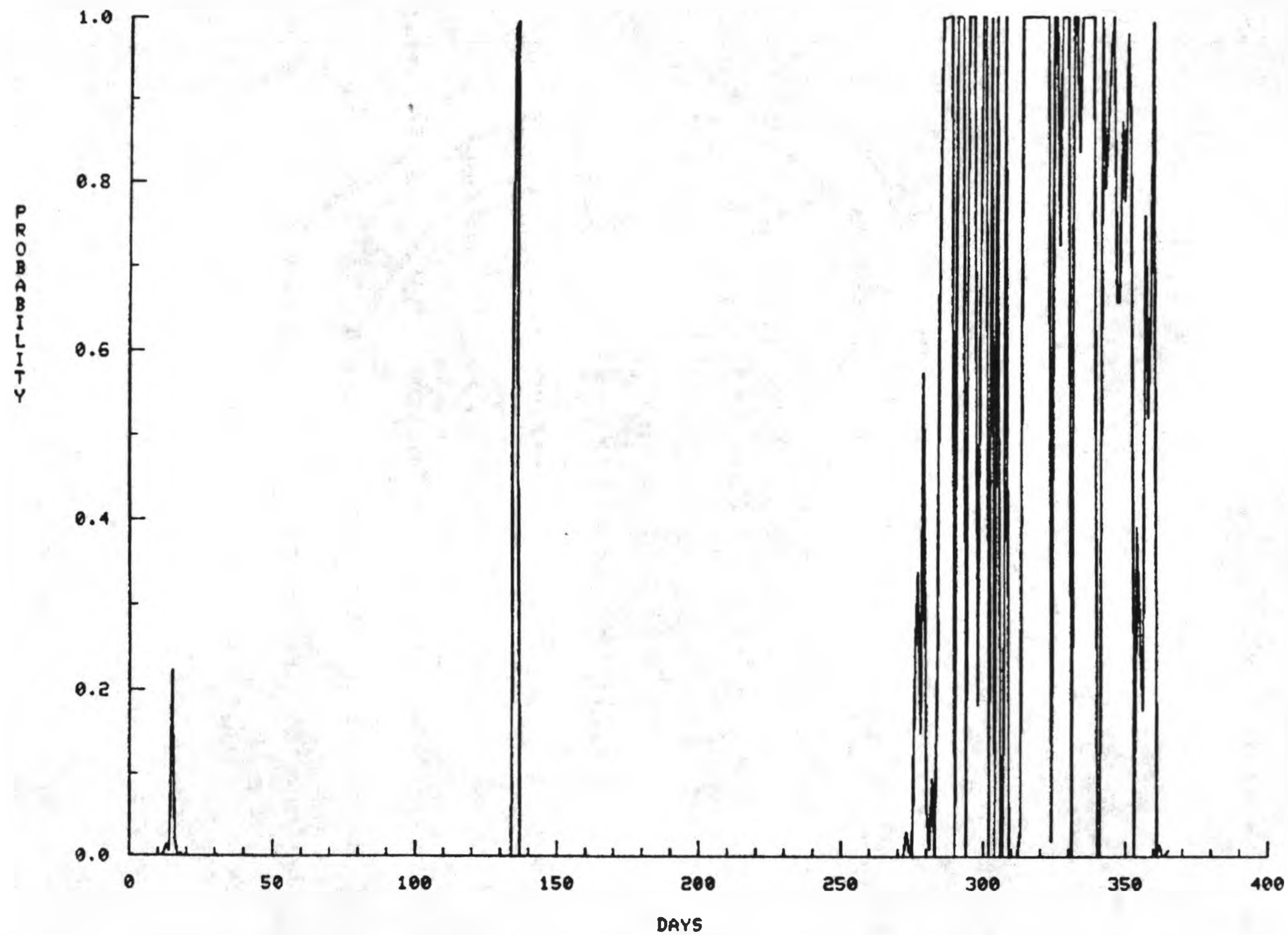

Figure 3-3. Probability of boron stream standard violation for Henry's Fork River near Linwood, Utah, water year 1971.

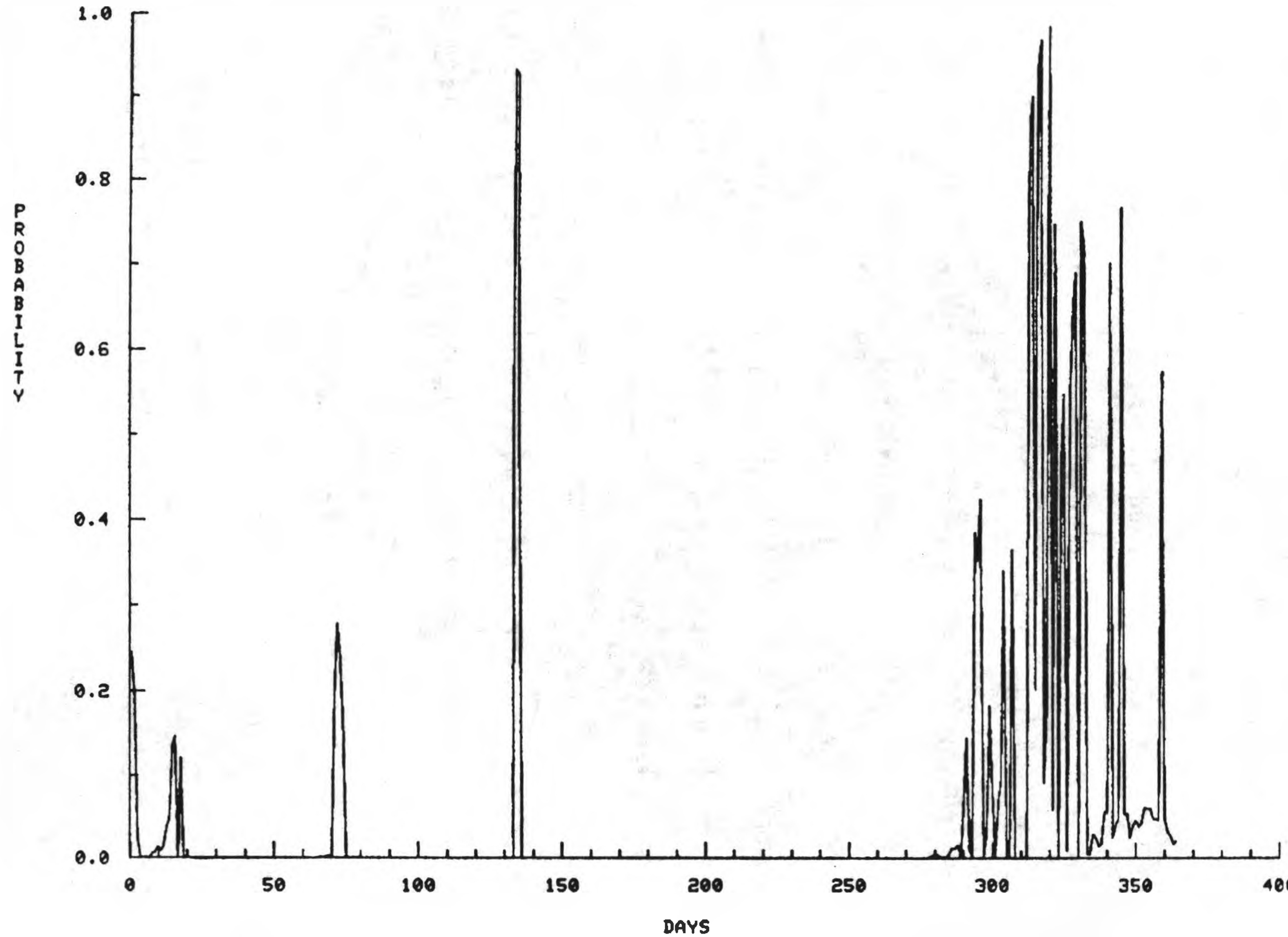

Figure 3-4. Probability of sulfate stream standard violation for Henry's Fork River near Linwood, Utah, water year 1971.

The detection of a change in the water quality system may be made by assessing the probability of collecting one or more samples equal to or greater than specified concentrations (Equation 3.24).

3.4.4.2 Summary

The procedure presented to estimate the conditional probability of a stream standard violation is simply the superimposition of a probability distribution on the residuals of a regression model. In the lumped data distribution procedure described in Section 3.2, an entire series of independent water quality data were used to determine a probability distribution which would accurately model the behavior of a water quality variable. The information obtained from this type of analysis is the daily probability of a stream standard violation without regard to season, flow, conductivity, temperature, etc. The regression analysis of Section 3.3 defined the deterministic relationships between variables but did not account for a random or stochastic component. The conditional probability approach combines these techniques to provide a maximum amount of information.

The use of conditional probabilities allows the timely determination of water quality characteristics. Since discharge, conductivity, and temperature are easily monitored continuously, an assessment of water quality can be made virtually every day during critical periods. The use of discharge, conductivity, and temperature is suggested because these variables are currently monitored daily at many sampling locations, other variables such as pH and dissolved oxygen may also be monitored continuously and may further improve the regression model.

3.5 Water Quality Indexing

3.5.1 Background

3.5.1.1 General Comments

The communication of general water quality conditions and the effect of public expenditures on the improvement of water quality is an important aspect of water quality management. There is general agreement among water quality professionals that present descriptive techniques are not adequate and a need exists for a uniform and objective communication procedure (Thomas, 1976). Water quality indices have been suggested by numerous researchers to provide such a procedure. Indices previously developed include an index based on eight physical and chemical characteristics of water, Horton (1965), indices designed for specific beneficial uses, Stoner (1978), an index based upon the collective opinion of professionals, Brown et al. (1970) and others. Most indexing procedures consist of finding a weighted average or geometric mean of values assigned to the concentrations of the water quality variables included in the index.

3.5.1.2 Purpose

The purpose of this section is to present two indices, an index to reflect changes in water quality and an index to relate water quality data to stream standards. According to Harkins (1974), a water quality index should summarize water quality concisely and objectively and should inform administrators clearly of water quality trends. The first index presented here will provide a means of indicating changes in water quality by utilizing the conditional probability model of Section 3.4 and the second will provide a quasi-objective means of rating water quality based on established stream standards.

3.5.2 Methodology

3.5.2.1 Water Quality Change Index

A regression model calibrated with several years of background, fixed station/fixed frequency water quality data may be used as the basis for indexing changes in water quality variables. It is first necessary to calculate the residual series from samples collected over a specified interval of time, for example, one year.

$$Z_i = \hat{Y}_i - Y_i \tag{3.41}$$

where Z_i = residual of sample

$\hat{Y}_i$ = regression estimate of sample concentration

Y_i = measured sample concentration

i = sample counter.

A new variable, U, may be determined as the sum of the residuals.

$$U = \sum_{i=1}^{n} Z_i \tag{3.42}$$

where n = number of samples collected in a year.

Now define V as

$$V = \frac{U}{\sqrt{n\,\sigma_Z^2}} \tag{3.43}$$

where σ_Z^2 = residual variance of model calibration as determined in Section 3.4.2.

If the residual series is assumed to be normally distributed and stationary, V can be shown to be normally distributed with mean zero and variance unity. With these assumptions, the cumulative probability of V, (denoted P) may be found in a cumulative standard normal deviate table. The index proposed here is the cumulative probability of V minus 0.5 and multipled by 100.

$$\text{Index} = (P - 0.5) \times 100 \tag{3.44}$$

This index contains values from -50 to 50 where positive values suggest improving quality and negative values suggest degrading water quality. If no change has occurred in the water quality system, index values can be shown to be uniformly distributed over the range -50 to 50 (Mood et al., 1974, p. 202).

Hypothesis testing theory may now be used to make inferences regarding water quality changes from index values. A detailed discussion of hypothesis testing will not be presented here but the interested reader may consult the references cited in Section 3.2.1.1. Simply stated, in hypothesis testing one specifies the probability, α, of rejecting the null hypothesis when in fact it should have been accepted. This type of error is commonly referred to as a Type I error.

Applying this approach to the water quality change index requires the null hypothesis to be specified as an unchanged system and the alternative hypothesis as a changed system. The user must then specify α, the probability of incorrectly assessing water quality as changed, i.e., degraded or improved, when in fact it is unchanged. It is now necessary to find the critical values of the index, denoted $\pm\phi$, where water quality will be described as improved or degraded with the given significance level, α. Since index values are uniformly distributed, critical index values may be determined

$$\phi = \pm(50 - \frac{\alpha}{2}) \tag{3.45}$$

where ϕ = critical index values

α = chosen significance level expressed as a percentage.

Table 3-5 presents criteria for evaluating index values with the chosen significance level, α.

Table 3-5. Water quality change index evaluation.

Row	Index Value	Assessment
1	-50 to $-\phi$	Degraded water quality
2	$-\phi$ to ϕ	Unchanged water quality
3	ϕ to 50	Improved water quality

To illustrate this method, assume that α has been specified to be 10 percent. By Equation 3.45, the critical values of the index are -45 and +45. Using Table 3-5 it can be seen that calculated index values greater than or equal to +45 indicate improved water quality and index values less than or equal to -45 indicate degraded water quality. Furthermore, an assessment of improved or degraded water quality will be incorrectly made, when in fact the quality is unchanged, 10 percent of the time. The probability of correctly assessing water quality as changed is uncertain as it depends upon the magnitude of the change.

3.5.2.2 Stream Standard Compliance Index

Water quality is a multivariate system, and to determine compliance/noncompliance of a river with stream standards it is necessary to compare each individual constituent with the associated standard. The purpose of this section is to present a water quality index which expresses, in a single number, river compliance or noncompliance with stream standards. This work is similar to the index proposed by Stoner (1978) which is based upon variables and critical concentrations defined for specified beneficial uses in state stream standards documents.

As discussed in Chapter 2, most states have stream standards expressed as limiting concentrations not to be exceeded for variables important to specific uses. The index proposed in this section assigns water quality values from zero to 100 linearly as variable concentration varies from the stream standard to zero. For variable concentrations greater than the standard, the water quality value is specified as a constant zero. For standards expressed as a minimum value not to be exceeded, such as dissolved oxygen, this relationship is reversed, and for a two sided standard, such as pH, the water quality value function takes on a triangular shape. The linear relationship between concentration and water quality value is assumed for simplicity but other functions may be used for certain variables where justified. Beneficial aspects of small concentrations of certain variables are overlooked by this procedure but the capability of the index to indicate stream standard compliance is not hindered. The index of stream standard compliance is

$$\text{Index} = \left(\prod_{i=1}^{n} WQV_i \right)^{1/n} \tag{3.46}$$

where WQV = water quality value for variable i

n = number of variables included in stream standard for specific use.

This index contains values from 0 to 100 with nonzero values indicating compliance with stream standards. An index value of zero indicates that at least one variable is equal to or above its stream standard and the river is therefore out of compliance. Larger positive values are generally associated with waters of better quality.

The stream standards compliance index may be used with individual samples, regression estimates, or with average values calculated over some interval by any of the procedures suggested in preceeding sections. Probability distributions of either the lumped data or partitioned data varieties may be fitted to index values since the index value is a random variable. Regression modeling and the determination of conditional probabilities of stream standards noncompliance may also be performed. Daily estimates of stream standards compliance index values may be obtained by utilizing variable concentration estimates from multivariate regression models. The daily probability of an index value of zero may be obtained from the conditional probabilities of violation for each variable.

$$P_o = 1 - \prod_{i=1}^{n} (1 - P_i) \tag{3.47}$$

where P_o = probability of index value of zero given flow, conductivity, and temperature

P_i = conditional violation probability of variable i

n = number of variables.

By observing the probability of stream standard violations on a frequent basis, a management agency may be able to monitor rivers intensively during periods of likely violations.

3.5.3 Discussion

Stream standards represent society's wish to maintain waters of suitable quality for specific beneficial uses. It is the responsibility of water quality management agencies to determine compliance or noncompliance of rivers with stream standards and to assess changes in water quality. It is also the responsibility of management to communicate these findings to legislators and the public in a manner that is understandable to the lay person. The use of water quality indices may provide such capability.

3.6 Summary

Water quality standards as used by most states are expressed as limiting concentrations not to be exceeded. Water quality is, however, a stochastic process and there is always a probability that a standard is being violated even though average conditions may be acceptable. Data collected by fixed station/fixed frequency monitoring networks contain little information regarding when such violations occur. Indeed, unless a sample is collected at precisely the time a violation is occurring, it will go undetected. By incorporating water quality data into the calibration of statistical models, the relative frequencies of violations may be assessed even if they are not directly detected. Also, statistical models may allow the timely identification of periods of time when samples should be collected by utilizing available information regarding current river conditions. Statistical models provide additional information which may be used to assist management agencies in the operation of monitoring networks, general assessment of water quality, and communication of water quality to the public.

The most basic procedure discussed in the chapter is the use of lumped data probability distributions. These distributions may be used to determine the daily probability of a stream standard violation and the expected number of violations in a period of time. Since flow and a few other variables are measured more frequently than most water quality variables, the partitioning of data sets into groups associated with these variables is suggested for a more detailed determination of the probability of a violation at a certain time. These techniques require temporally independent data such as the data most often collected by routine fixed station/fixed frequency monitoring networks.

Multiple linear regression modeling and conditional probability modeling of stream standard violations require frequent measurement of indicator variables such as discharge, specific conductance, and water temperature. Multiple linear regression modeling allows the determination of the deterministic component of a variable's change in time based on the correlation structure of the variable with indicator variables. This technique is useful in the determination of annual and seasonal means, the likely range of concentration, and the identification of critical monitoring periods. The conditional probability technique is a combination of probability distribution modeling and regression analysis. This method may be used in the evaluation of daily probabilities of stream standard violations which are useful in determining the expected number of stream standard violations in a period of time and helpful in the operation of monitoring programs.

The two water quality indices presented allow stream standard compliance or noncompliance and water quality changes to be communicated to the general public in a simple, concise manner. The water quality change index uses the conditional probability technique as a basis from which changes may be quantitatively assessed. The stream standards compliance index simply communicates compliance/noncompliance of river water with stream standards and may be used with probability distribution models, multivariate regression models, or conditional probability models to provide further information helpful to management agencies.

Chapter 4

ILLUSTRATION OF STATISTICAL PROCEDURES: A CASE STUDY - THE LITTLE WABASH RIVER NEAR LOUISVILLE, ILLINOIS

4.1 Introduction

4.1.1 Background Information

This chapter will present an illustration of many of the methodologies suggested in Chapter 3. The analyses will be made using data collected by routine monitoring networks operated by the U.S. Geological Survey for the Little Wabash River near Louisville, Illinois. The results of the analyses will be compared to a daily record of water quality variables collected during the water year 1977 by the Illinois State Water Survey. In this manner, some of the advantages and disadvantages of the various statistical techniques may be assessed. The work presented in this chapter is limited to an analysis of one year for four variables and broad generalizations may not be drawn based on this study alone.

The chapter is organized to follow the order the material is presented in Chapter 3 and most of the procedures are referenced from sections in that chapter. Each statistical procedure is briefly described and the data used in the analysis is identified. The results are summarized briefly and intermediate and final computations are presented in tables. Where appropriate, figures depicting the results are included. A brief summary for each procedure describes the relative merits and weaknesses of each analysis as indicated by the case study.

4.1.2 Data

Data sets used in the chapter are referred to in Table 4-1 which summarizes the contents of each set. U.S. Geological Survey records of chemical analyses collected approximately monthly at the Louisville station from 1970 to 1978, data set 1, are the principal data used in the statistical model calibration procedures. Data sets 2a and 2b are subsets of data set 1 associated with low and high flows respectively. Samples collected during flows of 250 cfs or less are included in data set 2a and other samples are included in data set 2b. The partitioning threshold of 250 cfs was chosen to split the data into groups with about one-third of the samples associated with high flows. This was done to provide more samples and thus better definition for low flow conditions when water quality is often most critical. U.S. Geological Survey daily records of discharge, specific conductance, and water temperature for water year 1977, data set 3, are used in the data generation models. The Illinois State Water Survey collected a daily record of water quality variables for the water year 1977, data set 4, and these data were used to compare the results of the analyses made with U.S. Geological Survey data. A sample of 12 days were arbitrarily selected from the Illinois data, the 15th day of each month for the year, to provide a typical state water quality record for the particular year, data set 5 (Table 4-2). Data collected by the U.S. Geological Survey would have been better suited for this purpose but no monthly chemical analyses were made by the agency in 1977. Field and laboratory procedures were assumed to be consistent for state and federal data for purposes of this work.

Table 4-1. Data used in case study.

Data Set	Agency	Period of Record	Number of Samples	Frequency	Variables
1	U.S.G.S.	1970-78	79	Monthly	Alk, Hardness, Mn, TDS
2a	U.S.G.S.	1970-78	45	Monthly	Alk, Hardness, Mn, TDS
2b	U.S.G.S.	1970-78	25	Monthly	Alk, Hardness, Mn, TDS
3	U.S.G.S.	1976-77	271	Daily	Flow, Conductivity, Temperature
4	Illinois State	1976-77	365	Daily	Alk, Hardness, Mn, TDS
5	Illinois State	1976-77	12	Monthly	Alk, Hardness, Mn, TDS

Table 4-2. Data Set 5.

Date	Alkalinity (mg/l)	Hardness (mg/l)	Mn (ppb)	TDS (mg/l)
Oct. 15, 1976	108	142	450	198
Nov. 15	142	196	510	--
Dec. 15	254	286	230	--
Jan. 15, 1977	282	328	490	--
Feb. 15	44	94	380	197
Mar. 15	92	144	300	237
Apr. 15	216	298	280	415
May 15	200	246	250	360
June 15	256	282	650	369
July 15	120	140	490	214
Aug. 15	190	216	720	331
Sep. 15	92	124	270	220
Mean	166.33	209.50	418.33	282.33
Standard Deviation	77.12	80.06	160.90	85.52
Coefficient of Skew	.036	.054	.585	.435

The water quality variables alkalinity, total hardness, manganese, and total dissolved solids (residue at 180°C) were selected for analysis. These variables were collected by both state and federal agencies and had fairly complete records at the Louisville location. Each of these variables have standards suggested in the "Red Book" (EPA, 1976) which were used to represent typical stream standards.

4.2 Probability Distribution Analysis

4.2.1 Modeling Procedure

The determination of probability distributions to model the behavior of water quality variables begins with the calculation of sample statistics. The sample mean, standard deviation, and coefficient of skew were calculated for data sets 1, 2a, 2b, and 5 and are presented with selected models in Table 4-3. Model selection was based on the coefficient of skew criteria suggested in Table 3-3. For simplicity, distribution parameters were calculated using the method of moment estimators provided with the probability distribution description of Section 3.2.2 and are shown in Table 4-4. The parameter, β, of the Gumbel distribution was calculated using Equation 3.17 since the four variables used in the analysis have standards expressed as maximum concentrations not to be exceeded. If the Gumbel distribution were to be used to model a variable with a standard expressed as a minimum concentration not to be exceeded, Equation 3.18 should be used.

The daily probability of a stream standard violation may be directly estimated using the probability distributions determined for data sets 1 and 5 by using Equation 3.21a

$$P[V] = \int_{s}^{\infty} f_X(x)\, dx \ . \tag{3.21a}$$

Table 4-3. Sample statistics for data used in case study.

Variable	Standard	Data Set	n	$\bar{x}$	$\hat{\sigma}$	$\hat{g}$	Selected Distribution
Alkalinity	300 mg/ℓ	1	55	155.09	58.08	.10	Normal
		2a	32	179.50	52.79	-.28	Normal
		2b	23	121.13	47.77	.68	Gamma
		5	12	166.33	77.12	.04	Normal
Hardness	300 mg/ℓ	1	55	215.64	69.68	-.03	Normal
		2a	32	236.59	67.08	-.35	Normal
		2b	23	186.48	63.64	.35	Gamma
		5	12	209.50	80.06	.05	Normal
Manganese	1000 ppb	1	66	263.73	201.14	1.37	Gumbel
		2a	42	319.88	213.57	1.29	Gumbel
		2b	24	165.46	131.10	.54	Gamma
		5	12	418.33	160.90	.59	Gamma
TDS	500 mg/ℓ	1	56	323.29	94.69	.21	Gamma
		2a	40	340.83	95.50	-.01	Normal
		2b	16	279.44	69.11	.11	Gamma
		5	9	282.33	85.52	.44	Gamma

Table 4-4. Parameters used in probability distribution modeling of case study data.

Variable	Data Set	Distribution	$\hat{\mu}$	$\hat{\sigma}$	$\hat{\lambda}$	$\hat{\eta}$	$\hat{\alpha}$	$\hat{\beta}$
Alkalinity	1	Normal	155.09	58.80	--	--	--	--
	2a	Normal	179.50	52.79	--	--	--	--
	2b	Gamma	--	--	0.0531	6.43	--	--
	5	Normal	166.33	77.12	--	--	--	--
Hardness	1	Normal	215.64	69.68	--	--	--	--
	2a	Normal	236.59	67.08	--	--	--	--
	2b	Gamma	--	--	0.0460	8.59	--	--
	5	Normal	209.50	80.06	--	--	--	--
Manganese	1	Gumbel	--	--	--	--	156.77	173.22
	2a	Gumbel	--	--	--	--	166.46	223.78
	2b	Gamma	--	--	0.0096	1.59	--	--
	5	Gamma	--	--	0.0162	6.76	--	--
TDS	1	Gamma	--	--	0.0361	11.66	--	--
	2a	Normal	340.83	95.50	--	--	--	--
	2b	Gamma	--	--	0.0585	16.35	--	--
	5	Gamma	--	--	0.0386	10.90	--	--

For the distributions used in this work, however, evaluating the exceedence probability of a stream standard with the cumulative distribution is a more simple task.

$$P[V] = 1 - F_x(s) \tag{4.1}$$

where $F_x(s)$ = cumulative probability distribution evaluated at the stream standard, s.

The cumulative distribution of the normal may be evaluated by finding the cumulative probability of the standard normal deviate, Z, in a table.

$$Z = \frac{s - \mu}{\sigma} \tag{4.2}$$

where Z = standard normal deviate
s = stream standard
μ = population mean (sample mean may be substituted as an approximation)
σ = population standard deviation (sample standard deviation may be substituted as an approximation).

The cumulative gamma distribution may be evaluated using a chi-square table. Enter the table with

$$v = 2\hat{\eta} \tag{4.3}$$

and

$$\chi^2 = 2\hat{\lambda}s \tag{4.4}$$

where v = degrees of freedom

χ^2 = chi-square value

$\hat{\eta}$ = gamma distribution parameter

$\hat{\lambda}$ = gamma distribution parameter

s = stream standard concentration.

The cumulative Gumbel distribution for maximum values is expressed

$$F_x(s) = \exp[-\exp(-w)] \tag{4.5}$$

and for minimum values

$$F_x(x) = 1 - \exp[-\exp(w)] \tag{4.6}$$

where $$w = \frac{x_i - \beta}{\alpha} \tag{3.12}$$

These distributions may be evaluated at a stream standard by substituting the stream standard concentration for x_i in Equation 3.12.

The estimation of the daily probability of a stream standard violation using flow-partitioned data, data sets 2a and 2b, may be accomplished in a manner similar to the unpartitioned case. It is first necessary to evaluate the cumulative distributions for each data subset and determine the exceedence probability of the standard as described above. The daily probability of a violation may then be determined as

$$P[V] = \left(\frac{N - n}{N}\right) P_a[V] + \left(\frac{n}{N}\right) P_b[V] \tag{4.7}$$

where N = total number of days in interval

n = number of days with flows above partitioning value

$P_a[V]$ = violation probability for low flows

$P_b[V]$ = violation probability for high flows.

The daily probability of a stream standard violation for a particular variable is an indication of the water quality with respect to the variable. Another indication of water quality is the expected number of days the river is in violation with a stream standard. This may be estimated by multiplying the daily violation probability by the number of days in the interval. The daily probability of a stream standard violation, the expected number of violations, and the actual number of violations for the variables used in this analysis for the Little Wabash River near Louisville, Illinois, water year 1977, are summarized in Table 4-5.

Table 4-5. Comparison of expected number of violations and observed number of violations.

Variable	No. of Days of Historic Record	Actual No. of Violations	Expected No. of Violations	Daily Violation Probability	Probability Model
Alkalinity	365	18	2.30	.0063	1
	365	18	3.61	.0099	2
	365	18	15.15	.0415	3
	271	18	0	0	4
	271	18	6.18	.0228	5
Hardness	365	69	41.25	.1130	1
	365	69	56.36	.1544	2
	365	69	47.16	.1292	3
	271	69	57	.2103	4
	271	69	60.77	.2242	5
Manganese	365	26	1.86	.0051	1
	365	26	2.92	.0080	2
	365	26	1.06	.0029	3
	271	25	0	0	4
	271	25	21.87	.0807	5
Total Dissolved Solids	246	0	10.97	.0446	1
	246	0	10.95	.0445	2
	246	0	3.62	.0147	3
	230	0	0	0	4
	230	0	0	0	5

1) Lumped data probability distribution
2) Flow-conditioned probability distribution
3) Annual sample probability distribution
4) Multipe linear regression
5) M.L.R.-conditioned distribution.

4.2.2 Results

In general, the best estimate of the expected number of stream standard violations was obtained (of the three probability distribution models) by the flow-conditioned distributions and the annual sample distributions. In Table 4-5 it may be seen that these two methods generally had better agreement with the observed number of violations than the lumped data distributions. This result may be expected because the flow-conditioned and annual sample distributions utilized information from the year in question and the lumped data distributions do not. All three methods underestimated the number of violations for alkalinity, hardness, and manganese and overestimated for total dissolved solids. The sample data when compared individually with stream standards detected no violations for alkalinity, hardness, or total dissolved solids and only one violation of hardness. The probability of violation is greater for low flow distributions than for high flow distributions for all variables.

The probabilities of obtaining the sample series for each variable, data set 5, from the distributions determined for the lumped data, data set 1, were estimated utilizing the procedure suggested in Section 3.2.4.1. The maximum and minimum values of each variable in the sample set were identified and the cumulative probability and exceedence probability were computed respectively. The probability of all samples being less than the maximum and greater than the minimum concentrations of the samples may be obtained by substituting the cumulative probability and exceedence probability into Equation 3.24.

$$P[X_{max} = max] = (F_x(X_{max}))^n \tag{4.8}$$

$$P[X_{min} = min] = (1 - F_x(X_{min}))^n \tag{4.9}$$

where $P[X_{max} = max]$ = probability that the maximum of a random series is equal to or less than observed maximum.

$P[X_{min} = min]$ = probability that the minimum of a random series is equal to or less than observed minimum.

$F_X(x)$ = cumulative distribution evaluated at X

n = number of samples.

The results of this analysis for the Little Wabash River are summarized in Table 4-6, and indicate the samples collected for alkalinity, hardness, and TDS were not unlikely samples to be drawn from their respective distributions. The sample series of manganese concentrations, with a minimum value of 230 ppb, however, could be expected to be drawn from the lumped data distribution of manganese less than one time in a thousand suggesting a likely change in the behavior of this variable.

4.2.3 Summary

The lumped data distribution method, probably, most accurately describes the average behavior of water quality variables of the probability models suggested in Chapter 3 because it incorporates all samples regardless of conditions existing at the time of sampling. However, as seen from the results of the Little Wabash River study, this technique may not be expected to produce accurate indications of water quality in any one particular year. The lumped data distribution may serve as an overall indication of water quality and may be used with annual sample data to indicate extreme water quality events. The flow-conditioned probability distribution method utilizes partitioned samples collected at monitoring locations and may be expected to yield better estimates of violation probability on a yearly basis than the lumped data distribution. Annual sample data, as shown in the case study, may not be expected to directly detect stream standard

Table 4-6. Probability of randomly collecting samples with the maximum and minimum values found in data set 5.

Variable	Number of Samples	Maximum Concentration (mg/ℓ)	Minimum Concentration (mg/ℓ)	Probability of all Samples less than Maximum	Probability of all Samples greater than Minimum
Alkalinity	12	282	44	.840	.712
Hardness	12	328	94	.518	.610
Manganese	12	0.51	0.23	.247	.000
Total Dissolved Solids	9	415	197	.204	.504

violations. Annual samples may provide useful information when used with probability distributions, however, to estimate the frequency of violations and to detect unusually high or low sample concentrations.

4.3 Multiple Linear Regression Analysis

4.3.1 Modeling Procedure

Multiple linear regression models were developed for the Little Wabash River near Louisville, Illinois using U.S. Geological Survey data. Models were developed to predict daily concentrations of alkalinity, hardness, manganese, and total dissolved solids based on daily records of discharge, specific conductance, and water temperature. Data used in the calibration procedure included daily average flow, conductivity, and temperature (data set 3) and grab samples of the four predicted variables (data set 1). The BMD02R stepwise regression computer program was used to determine the parameters of the models. This program also calculates the total squared correlation coefficient, r^2, of the model which was used to determine the best fitting transformation of Equations 3.26-3.29. A summary of best fitting transformations, model correlation coefficients, and model parameters for the Little Wabash River near Louisville, Illinois is found in Table 4-7.

4.3.2 Results

Data generations of daily concentrations of alkalinity, hardness, manganese, and total dissolved solids were made for the water year 1977 and compared with actual daily records collected by the Illinois State Water Survey (Figure 4-1 to 4-4). The hardness data generation was found to be shifted up significantly from actual observations and this discrepancy is thought to be due to differing analytical procedures used by the state and federal agencies responsible for the data

Table 4-7. Multiple linear regression model parameters calculated from data set 1.

Y	β_1	β_2	β_3	β_4	Transformation of Y	Transformation of X's	r^2
Alkalinity	-.00747	.27686	1.50465	-.89111	None	None	.7371
Hardness	-.00400	.37868	-.17609	27.09279	None	None	.9191
Manganese	-.27866	.37223	-.52241	2.79824	Log 10	Log 10	.3944
Total Dissolved Solids	.00187	.87158	-.01652	.16279	Log 10	Log 10	.9544

$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4$

where X_1 = discharge (or log 10 discharge) (cfs)

X_2 = specific conductance (or log 10 specific conductance) (μmhos/cm at 25°C)

X_3 = water temperature (or log 10 water temperature) (°C for no transformation and °F for log 10 transformation)

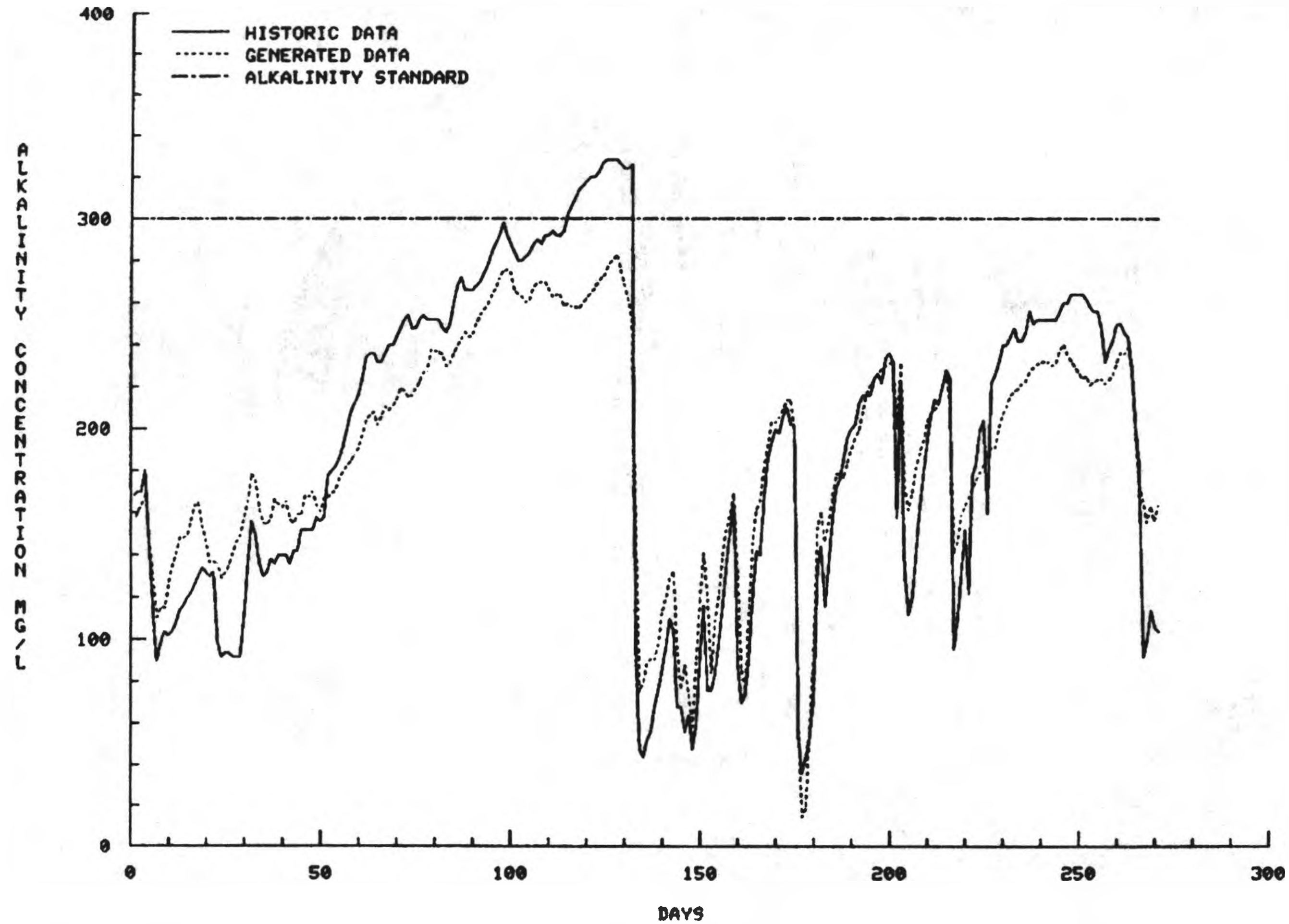

Figure 4-1. Multiple linear regression generation of alkalinity concentration for the Little Wabash River near Louisville, Illinois, water year 1977.

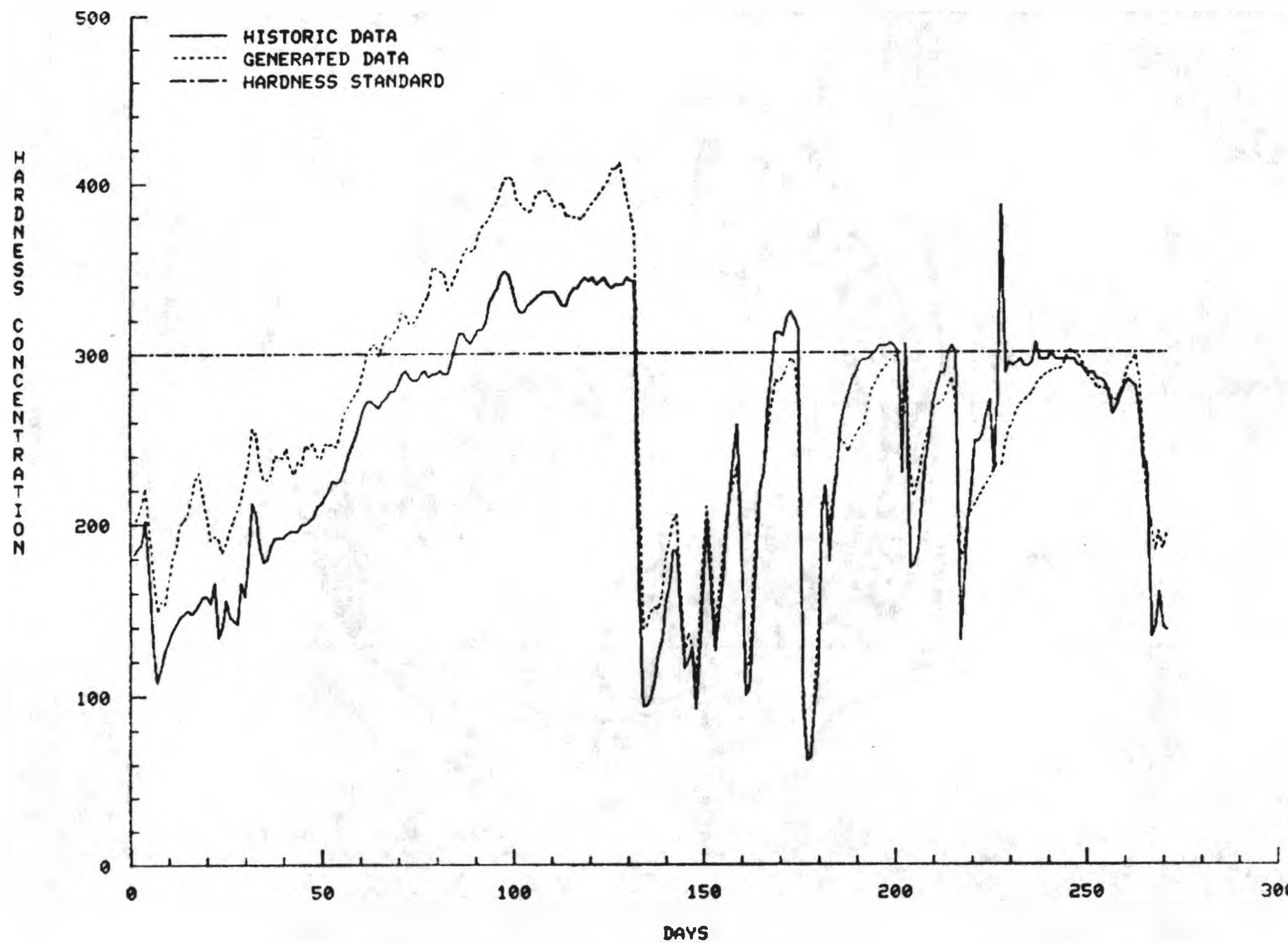

Figure 4-2. Multiple linear regression generation of hardness concentration for the Little Wabash River near Louisville, Illinois, water year 1977.

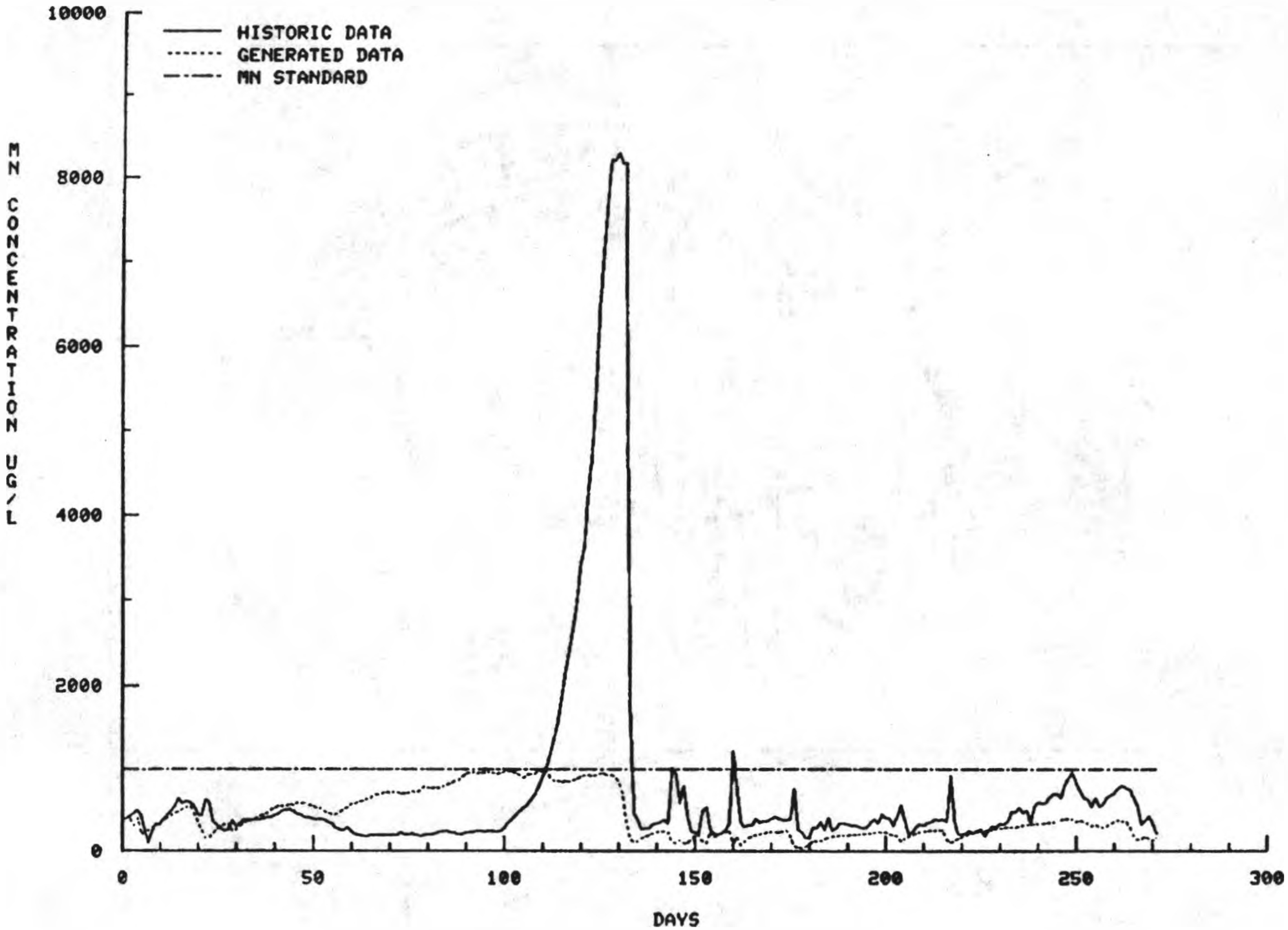

Figure 4-3. Multiple linear regression generation of manganese concentration for the Little Wabash River near Louisville, Illinois, water year 1977.

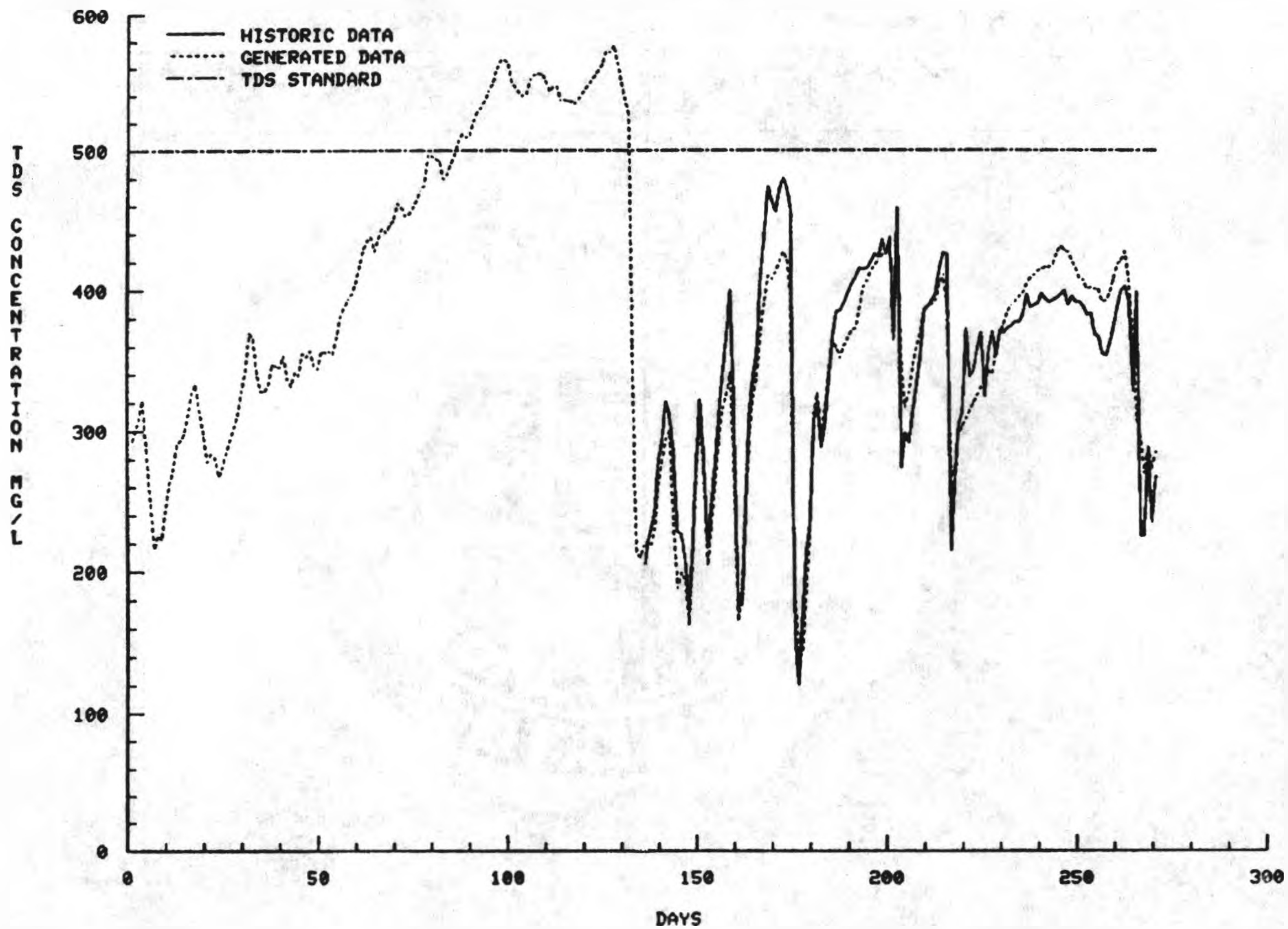

Figure 4-4. Multiple linear regression generation of total dissolved solids concentration for the Little Wabash River near Louisville, Illinois, water year 1977.

The number of days regression estimates are above a stream standard is a method of determining the expected number of stream standard violations in an interval of time, a summary of the expected number and actual number of violations for the data used in this analysis is found in Table 4-5. Mean concentration determined by averaging daily model estimates and averaging the sample data of data set 5 are compared to observed annual mean concentrations of alkalinity, hardness, manganese, and total dissolved solids in Table 4-8. It can be seen that annual mean concentrations were consistently estimated most accurately by averaging regression estimates.

Table 4-8. Annual mean concentration estimates.

	Sample Data (Data Set 5)	Regression Estimates	Actual Observations
Alkalinity	166.33 mg/ℓ	190.33	192.51
Hardness	209.50 mg/ℓ	264.92	243.39
Manganese	418.33 ppb	429.16	744.98
Total Dissolved Solids	282.33 mg/ℓ	343.71	346.47

4.3.3 Summary

Multiple linear regression modeling may be used to simulate water quality variable records based upon daily records of discharge, specific conductance, and water temperature. As seen in the analysis of the Little Wabash River, the model indicates periods of time when stream standard violations are likely to be occurring. If a principal objective of a water quality monitoring program is the detection of violations, regression modeling may provide current information regarding when samples should be collected. As a general indication of water quality with respect to a stream standard, the expected number of violations occurring in an interval may be estimated with a multivariate regression model. The indication of extreme events due to spills, accidents, etc. may not be accurately simulated by a regression model unless conductivity values respond substantially to the event. However, the model may be expected to partially respond to such events and indicate the need to monitor even if simulated values are significantly lower than actual concentrations. Estimates of mean annual concentration, more accurate than from annual sample data, may be obtained by averaging regression model estimates.

4.4 Conditional Probability Analysis

4.4.1 Modeling Procedure

Conditional probability models based on multivariate regression models were developed for alkalinity, hardness, manganese, and total dissolved solids for the Little Wabash River near Louisville, Illinois. The multiple linear regression models developed in Section 4.3 serve as the basis for the following work. The residual series was calculated by Equation 3.32 for each model with the data used in the calibration procedure and the residual means and variances were determined. For the conditional probability model of Equation 3.35 to be valid, the residual series must be normally distributed and independent. The normality requirement was tested using the chi-square "goodness of fit" criteria with six class intervals at the 10 percent significance level. Independence was checked by comparing the correlation coefficients between the residual series and other variables with the 95 percent probability limits of independent correlation coefficients (Jenkins and Watt, 1969).

$$r' = \pm \frac{1.96}{\sqrt{N}} \tag{4.10}$$

where r' = probability limits

N = number of samples.

The hypothesis that $r = 0$ is accepted if the calculated correlation coefficient falls within the limits of Equation 4.10. A summary of residual statistics is found in Table 4-9.

4.4.2 Results

The hypothesis of residual series normality, tested with the chi-square "goodness of fit" criteria, was accepted for each residual series at the 10 percent significance level. The test of residual independence was accepted for each variable except observed concentration, Y. Independence with this variable is not a model requirement and the effect of dependence is accounted for in the noise variance term, $\xi\,\sigma_Z$, of Equation 3.35. It is desirable, however, to remove this dependence, if possible, by utilizing transformations other than those used in this work (Equations 3-26 to 3.29) and/or a nonlinear modeling approach. The effect of removing all variable dependence is to minimize the residual variance and thus best define the process. The scope of this research did not allow the assessment of alternative modeling procedures.

The daily probabilities of stream standard violations for the four variables used in this analysis are plotted in Figure 4-5 to 4-8. The expected number of violations for each variable were calculated by summing daily violations probabilities and are shown in Table 4-5. It can be seen that of the procedures used in this case study, the expected number of violations were generally best estimated by the conditional

Table 4-9. Normality and independence check of residuals for conditional probability model.

Variable	N	$\bar{Z}$	σ_Z^2	$D^{(1)}$	$\chi^2_{3,.10}$	Accept/ Reject Normality	r					Independence Interval		Accept/ Reject Independence
							Q	U	T	Y	$\hat{Y}$	+r'	-r'	
Alkalinity	55	0	29.782	4.02	6.3	Accept	0	0	0	.513	0	.264	-.264	Accept[2]
Hardness	55	0	19.820	.31	6.3	Accept	0	0	0	.284	0	.265	-.264	Accept[2]
Manganese	64	0	.302	5.19	6.3	Accept	0	0	0	.778	0	.245	-.245	Accept[2]
Total Dissolved Solids	56	0	.028	3.36	6.3	Accept	0	0	0	.214	0	.262	.262	Accept

[1] Calculated chi-square statistc.

[2] Independence accepted between residual series and all other variables except actual concentration, Y.

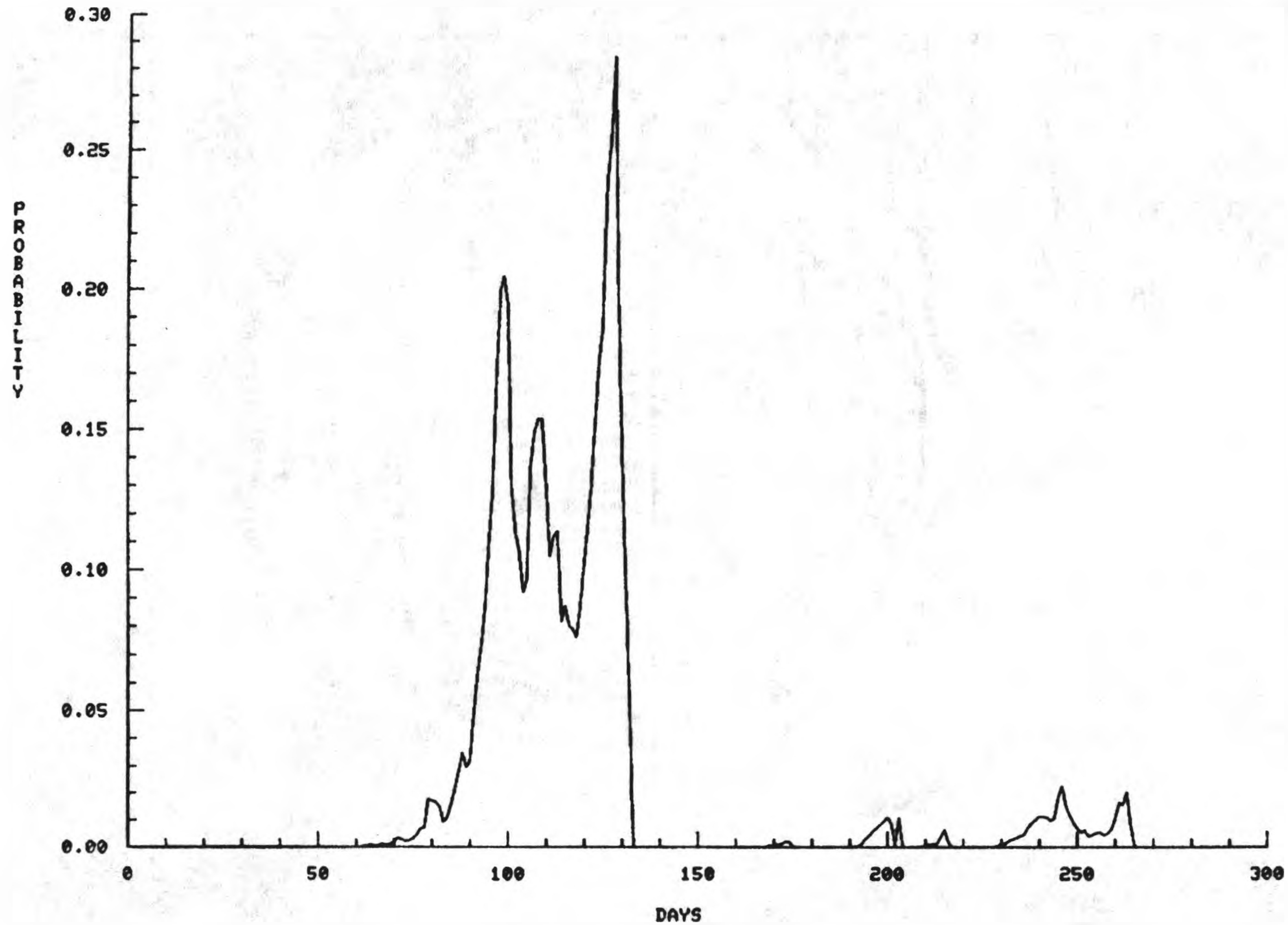

Figure 4-5. Probability of alkalinity stream standard violation for the Little Wabash River near Louisville, Illinois, water year 1977.

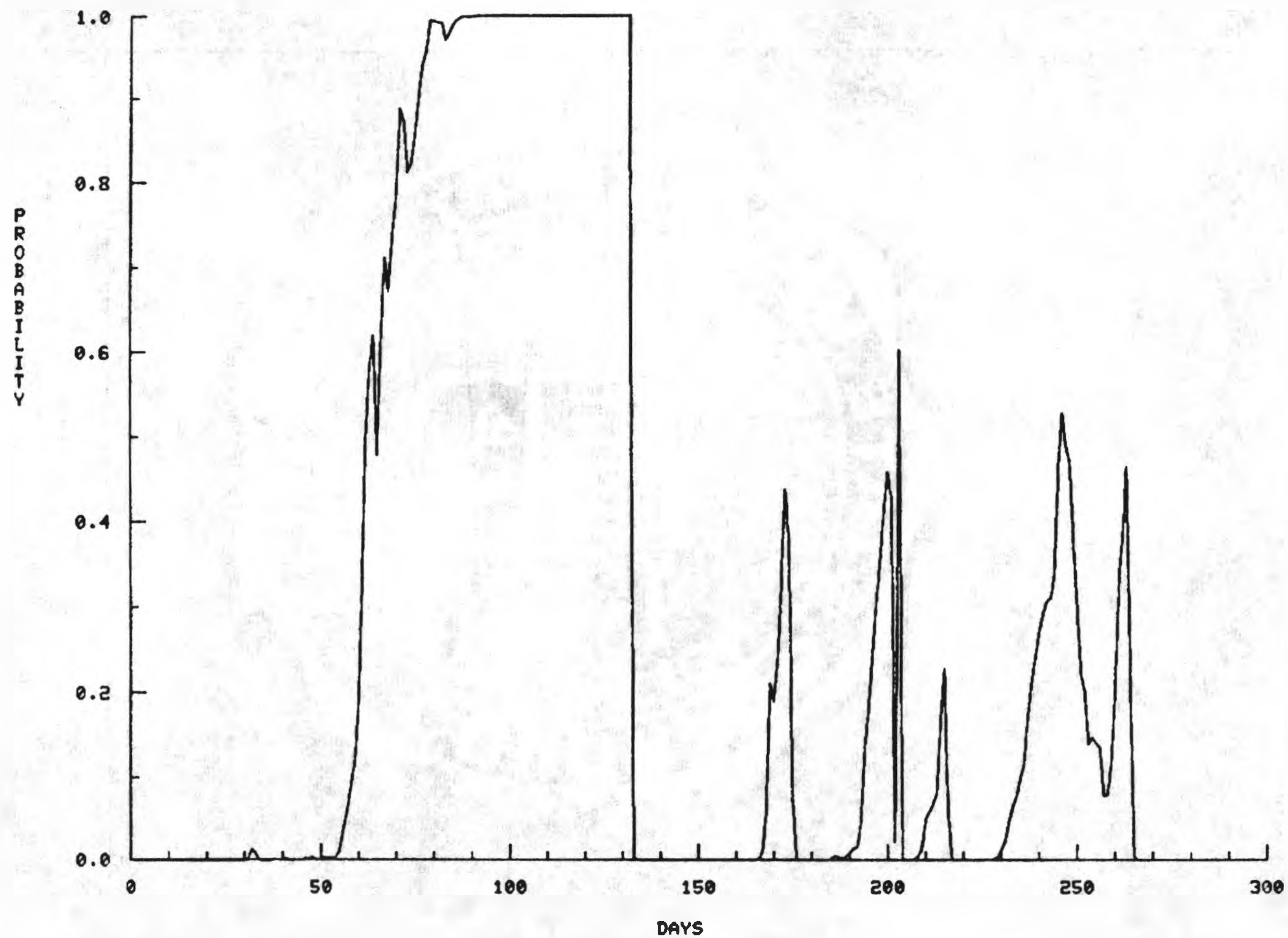

Figure 4-6. Probability of hardness violation for the Little Wabash River near Louisville, Illinois, water year 1977.

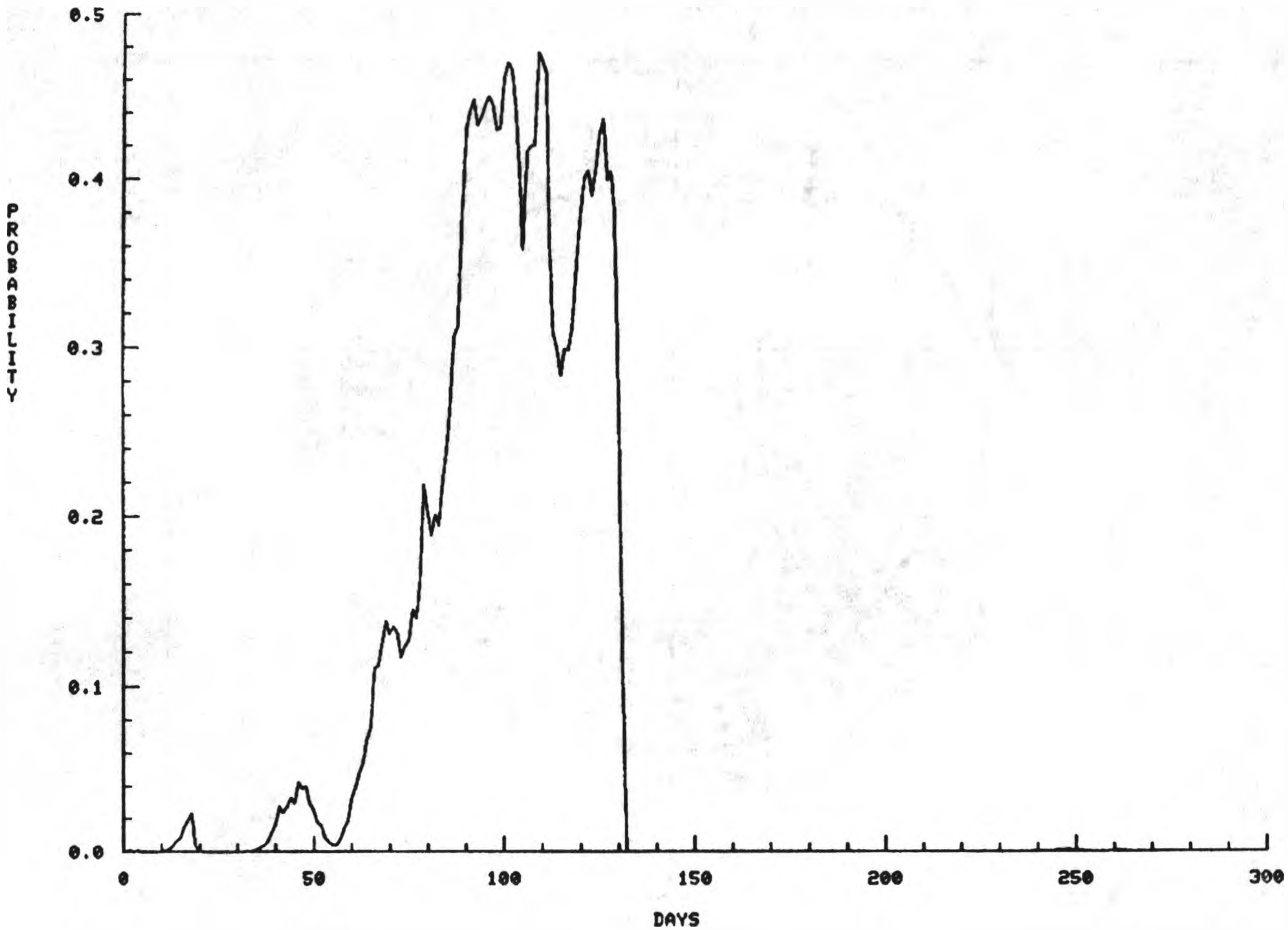

Figure 4-7. Probability of manganese violation for the Little Wabash River near Louisville, Illinois, water year 1977.

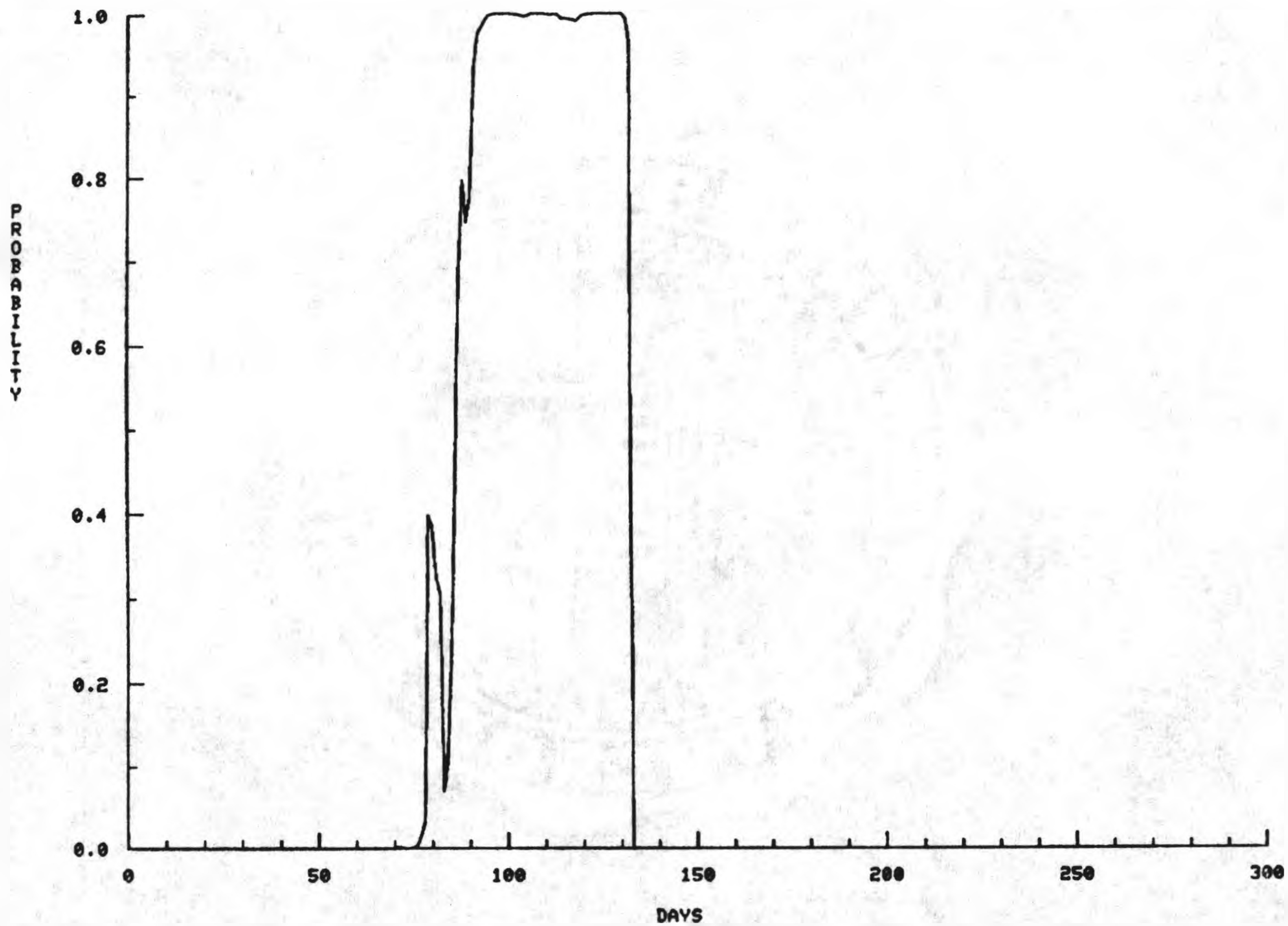

Figure 4-8. Probability of total dissolved solids violation for the Little Wabash River near Louisville, Illinois, water year 1977.

probability method. This may be expected due to the utilization of both information regarding conditions in the Little Wabash River during the year of the analysis and information regarding the historical behavior of each variable.

4.4.3 Summary

The conditional probability analysis of the Little Wabash River near Louisville, Illinois for the water year 1977 indicated periods of stream standard violations or near violations with relatively high violation probability. The conditional probability model was found to fit alkalinity, hardness, manganese, and total dissolved solids records acceptably well with the exception of residual series dependence with observed variable concentration. This problem is not critical to model performance. The expected number of stream standard violations were generally better estimated using this approach over other methods suggested in this report.

4.5 Water Quality Index Analysis

4.5.1 Change Detection Index

4.5.1.1 Procedure

The change detection water quality index presented in 3.5.2.1 was utilized with the conditional probability models developed in the previous section and a set of typical annual samples, data set 5, for the Little Wabash River. Residual series were calculated for each variable from regression model estimates and observed values as shown in Equation 3.41. A new variable, U, was calculated from each series as the sum of residuals. Since the residual series of each variable were shown to be normally distributed by the chi-square test of Section 4.4, the variables, U, are also normally distributed and may be standardized by Equation 3.43.

Table 4-10. Change detection index values for the Little Wabash River near Louisville, Illinois, water year 1977.

Sample Number	Alkalinity Residual	Hardness Residual	Manganese Residual (log)	TDS Residual (log)
1	32.27	46.94	-.0430	.0513
2	13.13	35.60	.0405	--
3	-38.67	33.52	.4822	--
4	-21.56	56.55	.2775	--
5	35.56	48.24	-.5053	.0455
6	25.48	21.77	-.4279	.0132
7	1.12	-17.83	-.1240	-.0136
8	-20.63	-38.73	-.0281	-.0437
9	-32.38	-1.33	-.2966	.0365
$U = \Sigma Z_i$	-5.68	184.73	-.6247	.0892
σ_Z^2	29.78	19.82	.302	.028
σ_U^2	268.04	178.38	2.718	.168
σ_U	16.37	13.36	1.649	.410
WQI	-13.68	50.00	-14.80	8.71

4.5.1.2 Results

Change detection index values calculated for the four variables are shown in Table 4-10. Using the critiera suggested in Table 3.5, only one variable, hardness, indicated a change at the 10 percent significance level. This result is probably attributable to differing laboratory or sampling procedures used by the state and federal data collection agencies and not to a change in hardness concentration behavior. Observed alkalinity and manganese concentrations were somewhat higher than would have been expected, as indicated by negative index values, suggesting the possibility of degrading water quality with respect to these variables. Observed total dissolved solids concentrations were somewhat lower than would have been expected indicating possible improving water quality with respect to this variable. Index values for alkalinity, manganese, and total dissolved solids were close enough to zero, however, to not clearly indicate improving or degrading water quality. The manganese violation event was not well indicated by the index because samples were not collected during the period of highest concentrations.

4.5.2 Stream Standards Compliance Index

4.5.2.1 Procedure

The stream standards compliance water quality index presented in Chapter 3 was calculated for each individual sample of data set 5 and the annual mean concentration for each variable as determined by averaging regression model estimates. Water quality values for the index were calculated using the linear relationship suggested in Section 3.5.2.2 and stream standards obtained from the Red Book (EPA, 1976). The stream standards used in this analysis are shown in Table 4-3. For convenience, the index was computed using a contrived set of variables consisting of those used in previous analyses. In actual practice the index would be calculated using all variables included in a state stream standards document corresponding to the beneficial uses designated for the particular river reach.

4.5.2.2 Results

The stream standards compliance index was computed for each sample in data set 5 and the annual mean concentration estimations based on regression model predictions and are shown in Table 4-11. The Little Wabash River was out of compliance one time out of 12 samples and was in compliance on an annual basis. Of the 11 monthly samples in compliance, index values ranged from 12.3 to 68.5 and averaged 41.75

Table 4-11. Stream standards compliance index values for the Little Wabash River near Louisville, Illinois, water year 1977.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	Annual mean
WQI	57.8	44.7*	17.7*	0*	68.5	60.4	12.3	30.3	16.9	55.3	31.4	63.9	29.55

*Calculated with only three variables because of missing data.

indicating water quality generally suitable for the designated river use. The index was also calculated on a daily basis using daily regression model predictions of alkalinity, hardness, manganese, and total dissolved solids as shown in Figure 4-9. The daily probability of an index value of zero was calculated according to the procedure suggested in Section 3.5.2.2 and is shown in Figure 4-10.

4.5.3 Summary

The results of the Little Wabash River change detection index analysis indicated no significant changes associated with alkalinity, manganese, or total dissolved solids concentrations. Significantly lower concentrations of hardness, evidenced by an index value of 50.00, were thought to be due to data aquisition inconsistencies. Data incorporated into the use of this index must be of consistent quality for meaningful analysis. The short-term pollution event of manganese was not well indicated by the index due to poorly timed sampling.

The results of the stream standard compliance index indicated the Little Wabash River was generally in compliance in water year 1977 with the artificial management system used for illustrative purposes in this analysis. As shown in the preceeding work, the index may be used with regression models and conditional probability models to generate daily information assisting in the allocation of monitoring resources.

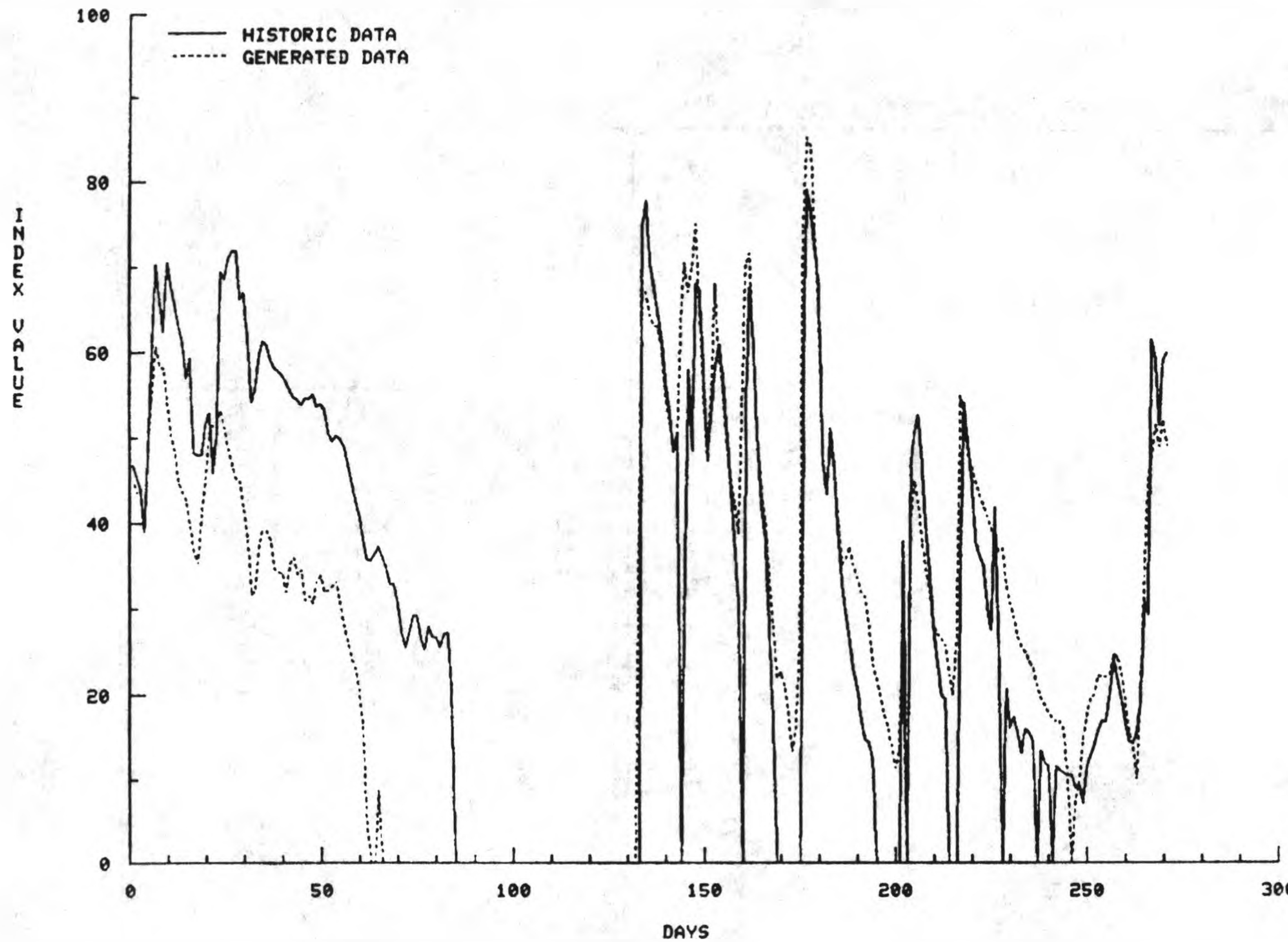

Figure 4-9. Multiple linear regression generation of stream standard compliance index values for the Little Wabash River near Louisville, Illinois, water year 1977.

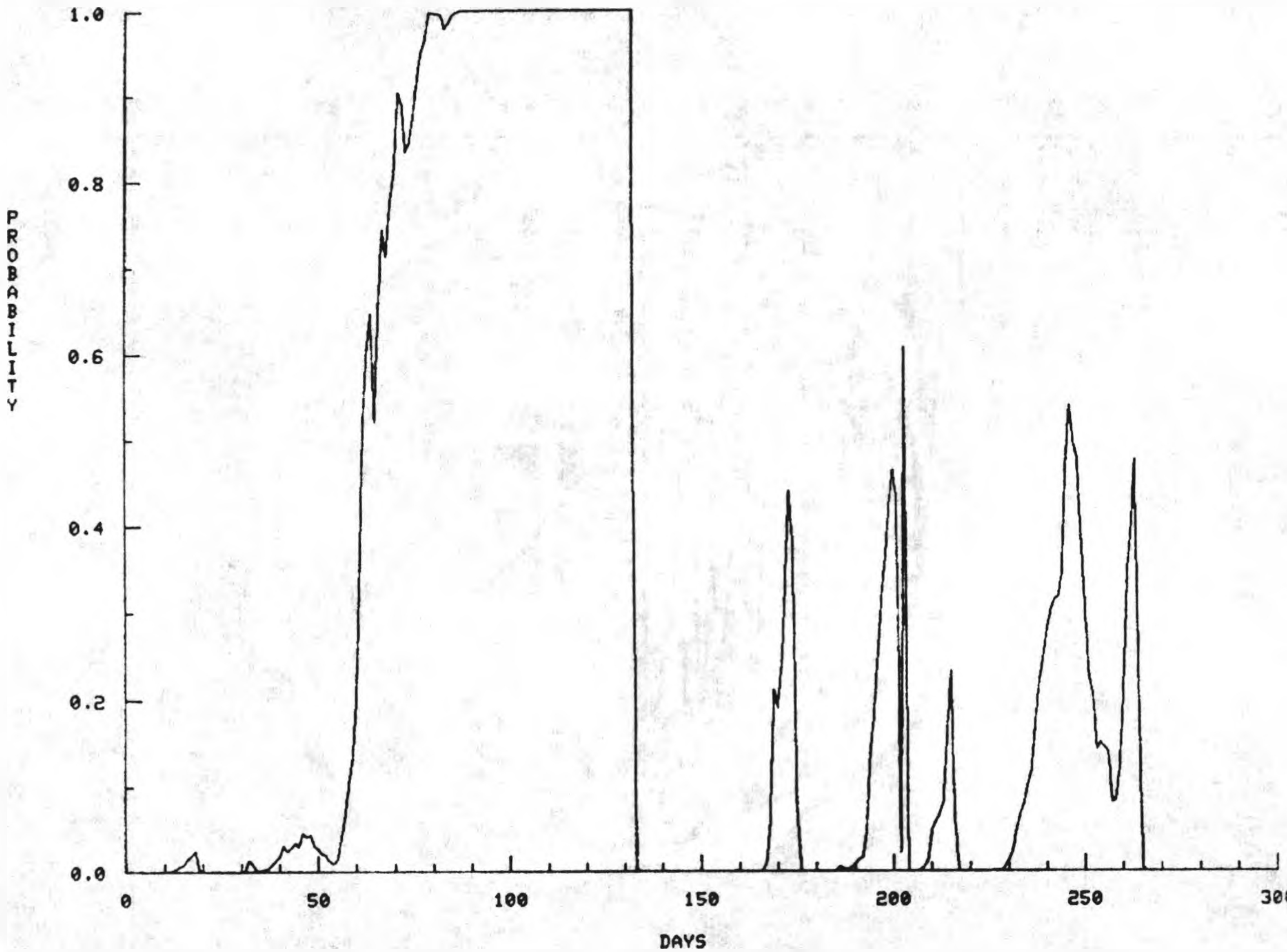

Figure 4-10. Probability of stream standard compliance index value equal to zero for the Little Wabash River near Louisville, Illinois, water year 1977.

Chapter 5

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary and Conclusions

Since the mid-1960's public concern over the quality of the environment has prompted remedial legislation at all levels of government. River water quality has been the focus of much environmental attention and considerable amounts of public money have been spent in attempting to assess and improve river quality. The federal government has required the states to promulgate stream standards, to determine compliance or noncompliance of surface waters with standards, and to assess improving or degrading water quality. Enforcement of acceptable water quality has been changed from in-stream monitoring to effluent permit monitoring due to the difficulty of determining parties responsible for violations by monitoring river conditions. Stream standards and monitoring remain an important aspect of state water quality management, however, in the assessment of the success of water quality efforts.

States have typically incorporated stream standards which include narrative standards, specific numeric criteria, and low flow stream standard exemption policies. The narrative standards generally apply to all surface waters and define critical levels of man-made pollutants such as oil and grease. Numerical criteria are established for variables considered important for designated beneficial uses assigned to each river reach in the state. Specific criteria are generally expressed as limiting concentrations not to be exceeded by the various constituents at any time except during critical low flows. The critical low flow criteria most often used by states is the seven day-ten year low flow.

River water quality is monitored by both federal and state agencies with the principal responsibility belonging to states. Typical monitoring networks consist of fixed station/fixed frequency sampling locations where numerous water quality variables are analyzed on approximately a monthly basis. Often variables are monitored for which no standard is specified and vice-versa. Intensive surveys are conducted to obtain detailed information regarding water quality at a specific location and time. Field and laboratory procedures for the aquisition of water quality information are referenced by federal guidelines.

The information provided by routine water quality monitoring networks is often of little use in determining overall compliance with limiting-concentration type stream standards and is often difficult to evaluate for trends. Water quality variables fluctuate in concentration in response to many factors and single point in time measurements convey little direct information regarding stream standard compliance. For this reason, many researchers in the field of water quality hydrology have suggested a change in emphasis of stream monitoring from the fixed station/fixed frequency approach to synoptic surveys. Synoptic surveys are expensive to conduct and yield information pertaining only to the specific location of the study and for these reasons have not been widely used.

Routinely collected water quality data, however, may be evaluated with respect to stream standards through the application of probability and statistical methods. The use of these methods is necessary for the meaningful evaluation of water quality because of the statistical nature of sampling. Water quality samples represent a series of realizations taken from a population and to make inferences regarding the population, the random behavior of water quality must be recognized and dealt with by appropriate analytical procedures. Many probability and statistical procedures are available for water quality evaluation and the purpose of this study was to illustrate the application of several such techniques.

Five probability and statistical procedures were chosen for the study: (1) probability distribution modeling of water quality variables, (2) multiple linear regression modeling, (3) conditional probability modeling of stream standard violations given current river conditions, (4) an index indicating changes in water quality, and (5) an index indicating compliance/noncompliance of water quality with stream standards. Each procedure is developed in the text and tested with a case study. The procedures have different data requirements, require different assumptions, and provide information suitable for different management needs.

The determination of probability distributions which model the behavior of water quality variables is a statistical technique which provides an estimate of the frequency of stream standard violations. The selection of a probability model to use in a given application may be made based on the coefficient of skew of the sample series. Distributions may be determined for data consisting of temporally independent samples collected during various conditions and represent the average behavior of a variable. Partitioning data into groups associated with differing conditions, such as high and low flow, allows a more accurate estimate of violation probability to be made for a specific period of time. The use of probability distribution models provides an overall assessment of water quality but does not provide information pertaining to when violations occur or the magnitude of violation events.

Multivariate regression models may predict water quality variable concentrations based on easily measured factors which affect water quality such as discharge, specific conductance, and temperature. These models may also serve as the basis for determining the probabilities of stream standard violations given current river conditions. Knowledge of when violations are likely to be occurring allows a management agency to optimize the utility of its monitoring resources. Conditional probabilities based on regression model estimates may also be used in conjunction with recently collected samples to assess changes in overall water quality.

The communication of water quality to the public in an easily understandable manner is an important task for water quality management agencies. The reporting of changes in water quality and compliance or noncompliance of rivers with stream standards is necessary to keep the public informed as to the effectiveness of public expenditures in the area of water quality improvement. The indices proposed in this study may provide simple, concise descriptive techniques suitable for this purpose.

5.2 Recommendations

5.2.1 General Comments

Water quality management objectives need to be clearly defined for the rational design of effective water quality management programs.

The selection of analytical procedures to use in the evaluation of water quality data depends on the objectives of the monitoring program. Data collection networks should be designed for the aquisition of data relevant to objectives and suitable for the probability and statistical procedures used in analysis. A combination of daily measurements of a few indicator variables, monthly measurements of all variables included in stream standards, and occasional intensive surveys conducted in response to suspected critical conditions should provide management with necessary information for the assessment of water quality. Due to the several monitoring programs at both the state and federal levels, it is not necessary for any one program to collect all the data. Coordination of monitoring efforts could greatly enhance the use of all data.

5.2.2 Future Research

The research conducted in this project is by no means complete. Further research is needed to more fully develop the procedures suggested in the report, to develop additional procedures, and to more fully assess the capabilities of probability and statistical modeling of routinely collected water quality data. Probability distribution modeling of negatively skewed data should be analyzed more appropriately than by the procedures used in this work. Both the transformation of data, for example, $Y = 1/x$, and the use of negatively skewed distributions should be evaluated. Also, criteria other than the sample coefficient of skew could be developed as a basis of probability model selection. This may be desirable because the coefficient of skew is often poorly estimated from sample data (Appendix B).

The multiple linear regression model used in this work is not necessarily the best model for the generation of water quality information from known river conditions. Other models should be evaluated for usefulness for this purpose. The indicator variables discharge, specific conductance, and water temperature were used in the regression models because they are often measured on a daily basis. Other variables may prove to be very useful indicators of important water quality constituents and should also be measured on a daily basis to provide more accurate regression estimates. A study to determine such variables is needed.

The "change detection" water quality index presented in this report may be made more useful by incorporating more than one year of index values into an assessment. Subtle changes in water quality may require the utilization of several years of change detection index values and modification of the hypothesis testing algorithm of Section 3.5.2.1 to incorporate n years of index values. Also, it would be interesting to use the index on a control system which could be programmed into the computer. The sensitivity of the index could then be assessed by creating changes in the control system of differing magnitudes.

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Appendix A

FREQUENCY AND DURATION OF DESIGN LOW FLOWS

A.1 Introduction

River water quality standards as written in the regulations of many states are not applicable during periods of very low flow. The selection of a design low flow, below which stream standards do not apply is an important practical aspect of a state's water quality management effort. Both frequency and duration of historical low flows are important considerations in the selection of appropriate design criteria. The purpose of this work is to determine the magnitude, frequency and average duration of three design low flows for several rivers in order to gain some understanding of how restrictive these design criteria are. Six streams located in the United States (Table A-1) in which daily flow data were readily available at Colorado State University were selected for the study. The streams have different watershed areas and characteristics and are located in various climatic and hydrologic regimes. The design critiera selected for analysis are the seven day-ten year low flow (7Q10), seven day-five year low flow (7Q5), and seven day-two year low flow (7Q2).

A.2 Methodology

The series of annual minimum 7 day flows were fitted to the two parameter log-normal distribution for each river by determining the sample mean and standard deviation. The n year recurrence flow was calculated with the following equation:

Table A-1. Stations used in design low flow analysis.

Station	Area (sq. mi)	Period of Record	Mean Daily Flow (cfs) Std. Dev. (cfs)	7-day Low Flow (cfs)		
				10 year	5 year	2 year
Tioga River near Erwins, New York	1,370	1921-60	1,379 2,778	34	41	62
McKenzie River at McKenzie Bridge, Oregon	345	1924-60	1,638 774	836	882	977
Boise River near Twin Springs, Idaho	830	1921-60	1,173 1,459	209	228	270
Madison River near West Yellowstone, Montana	419	1924-60	459 191	250	270	319
Oconto River near Gillett, Wisconsin	678	1921-60	544 441	173	190	228
Merced River at Pohono Bridge, California	321	1921-60	596 979	7	9	16

$$\log_{10} Q_n = \bar{X} - K(S)$$

where Q_n = discharge of recurrence interval n years

$\bar{X}$ = mean $\log_{10}$ of annual low flows

$$= \frac{1}{n} \sum_{i=1}^{n} \log_{10} X_i \qquad X_i = \text{7-day low flow for year}$$

S = standard deviation of $\log_{10}$ annual low flows

$$= \left[\frac{\sum_{i=1}^{n} (\log_{10} X_i - \bar{X})^2}{n - 1}\right]^{1/2}$$

n = number of years of record

K = normal distribution constant.

Values for K were taken from a cumulative standard normal deviate table and correspond to a cumulative probability of 90 percent for the ten-year flow, 80 percent for the five-year flow, and 50 percent for the two-year flow.

A.3 Results

The results of the study are tabulated in Table A-2. It was found that flows equal to or less than the 7Q10 occurred between 0.25 and 1 percent of the days for the six rivers used in the study. The average frequency of occurrence was 0.52 percent, the average frequency of years with at least one event (day with $Q \leq$ design Q) was 20.5 percent. Flows equal to or less than the 7Q5 occurred between 0.42 and 3.12 percent of the days with an average frequency of occurrence of 1.39 percent, an average duration of 7.5 days, and 29.5 percent of the years had at least one event. The 7Q2 criteria was achieved between 3.39 and 9.00 percent of the days for the six rivers with an average frequency

Table A-2. Results of design low flow analysis.

Station	7Q10			7Q5			7Q2		
	Event Frequency (% days)	Percent Years with at Least One Event	Average Duration of Events (days)	Event Frequency (% days)	Percent Years with at Least One Event	Average Duration of Events (days)	Event Frequency (% days)	Percent Years with at Least One Event	Average Duration of Events (days)
Tioga River	0.42	17.5	3.8	0.92	32.5	5.4	3.58	67.5	8.2
McKenzie River	0.27	16.2	3.7	3.12	27.0	14.1	8.89	56.8	27.3
Boise River	0.57	40.0	2.9	1.40	50.0	4.1	5.66	80.0	6.3
Madison River	0.97	21.6	6.9	1.23	24.3	7.9	9.00	54.1	10.0
Oconto River	0.60	22.5	6.7	1.34	32.5	8.5	6.62	70.0	9.9
Merced River	0.33	5.0	4.8	0.42	10.0	5.2	3.39	40.0	22.3
Average	0.52	20.5	4.8	1.39	29.5	7.5	6.12	61.5	14.0

of occurrence of 6.12 percent, an average duration of 14.0 days, and 61.5 percent of the years had at least one event.

A.4 Summary

From the results it is evident that the commonly used design flow, 7Q10, is quite restrictive because standards will be in effect 99.5 percent of days. At the same time, it is apparent that if an event occurs there is a high probability that it will persist for several days. Design flows of smaller return period are less restrictive in terms of frequency and tend to persist for longer periods.

Appendix B

EXPECTED ACCURACY OF ANNUAL STATISTICS CALCULATED FROM VARIOUS SAMPLING FREQUENCIES

B.1 Background

Most water quality data is collected from fixed station/fixed frequency monitoring networks. This data is often used for calculation of annual sample statistics from which water quality is assessed. Accuracy of sample statistics is a function of two factors, the variance of the process and the number of samples collected. Variables which have high variances require many samples to accurately estimate the population mean and variables with small variances require few. The purpose of this work is to indicate the average error which may be expected with the calculation of sample mean, standard deviation, and coefficient of skew from water quality samples collected at various sampling frequencies.

B.2 Methodology

Water quality records taken on a daily basis at ten Illinois monitoring locations for eight variables, in water year 1977, were used in the analysis. The population statistical parameters mean, standard deviation, and coefficient of skew were determined for each variable at each station. Representative samples of 36, 30, 24, 18, 12 and 6 per year were extracted from the daily records and sample statistical parameters were calculated. The percent error of sample statistics with population statistics were calculated and the average absolute value of these errors determined. Average absolute values of error percentage are shown with average coefficient of variation in Table B-1 for each variable.

B.3 Results

Figures B-1, B-2, and B-3 show the average error percentages for all data sets, average coefficient of variation 0.67, and for the variables with highest and lowest average coefficients of variation, 1.22 and 0.18 respectively, plotted versus sampling frequency. As expected, the greatest average errors are associated with data sets with greatest coefficient of variation and smallest average errors with data sets with small coefficient of variation. It can be seen that errors generally expected for sample estimates of skew are quite large, this presents problems in identifying appropriate probability distributions to model annual data. Average errors in samples means calculated from the commonly used 12 per year frequency ranged from 9.10 percent to 21.68 percent.

B.4 Conclusions

The errors associated with sample statistics based on a few samples per year are sufficiently large to cause seriously inaccurate conclusions to be drawn regarding water quality. For this reason, judgements made based on annual samples should be corroborated when possible by other means. Statistical models incorporating correlation between variables and/or intensive surveys should be used to substantiate results of annual samples before important water quality decisions are made.

Table B-1. Average absolute value of error percentage between sample and population statistics for water quality variables.

Variable	Average Coefficient of Variation	36 Samples/year			30 Samples/year			24 Samples/year			18 Samples/year			12 Samples/year			6 Samples/year		
		$\bar{X}$	$\hat{\sigma}$	$\hat{g}$	$\bar{X}$	$\hat{\sigma}$	$\hat{g}$	$\bar{X}$	$\hat{\sigma}$	$\hat{g}$	$\bar{X}$	$\hat{\sigma}$	$\hat{g}$	$\bar{X}$	$\hat{\sigma}$	$\hat{g}$	$\bar{X}$	$\hat{\sigma}$	$\hat{g}$
PO_4	1.12	9.90	24.48	45.94	9.83	25.34	45.60	11.52	27.48	49.29	13.99	29.59	54.56	15.07	32.63	61.87	21.52	40.66	76.40
Na	0.40	2.24	6.37	48.81	2.00	6.71	50.98	2.87	8.64	54.43	3.30	11.21	66.00	4.61	15.37	77.37	6.78	21.74	104.22
TOC	0.37	2.56	19.29	54.45	3.93	21.59	70.91	4.81	24.48	70.59	4.82	25.62	80.90	6.45	30.57	97.33	9.07	37.23	128.05
Hardness	0.18	1.00	8.09	39.27	0.88	9.39	41.00	1.37	10.72	56.18	1.47	12.91	60.96	2.37	15.44	82.17	3.55	21.90	188.87
Ammonia Nitrogen	1.12	5.21	11.06	20.27	5.94	11.22	20.29	6.42	12.37	21.91	8.27	14.30	25.90	11.29	19.40	31.75	20.36	32.68	48.33
NO_3	0.89	3.80	12.12	30.45	5.19	13.49	33.12	5.84	14.30	34.50	9.26	18.60	39.14	8.90	18.24	44.20	18.08	28.80	68.38
TDS	0.19	1.08	9.15	193.46	0.84	11.24	219.43	1.40	12.68	286.98	1.50	15.25	246.62	2.43	18.90	387.89	3.37	26.10	399.08
Fe	1.22	9.83	26.94	35.38	11.41	29.81	38.84	16.43	35.99	44.24	17.43	38.56	48.75	21.68	45.53	59.05	29.84	54.33	73.42
Average	0.67	4.45	14.69	58.50	5.00	16.10	65.02	6.33	18.33	77.27	7.51	20.76	77.85	9.10	24.51	105.20	14.07	32.93	135.84

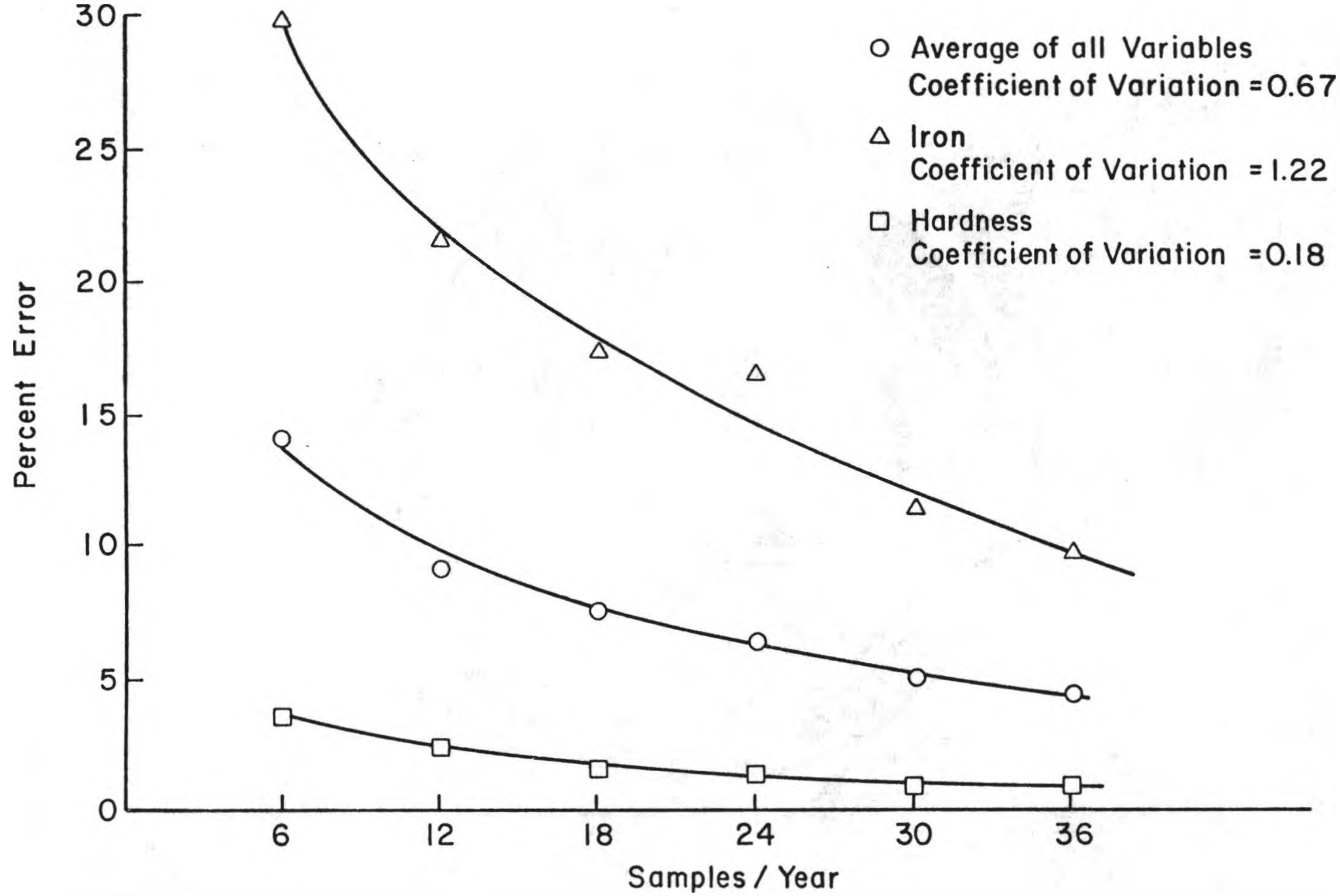

Figure B-1. Average absolute value of sample mean error percentage.

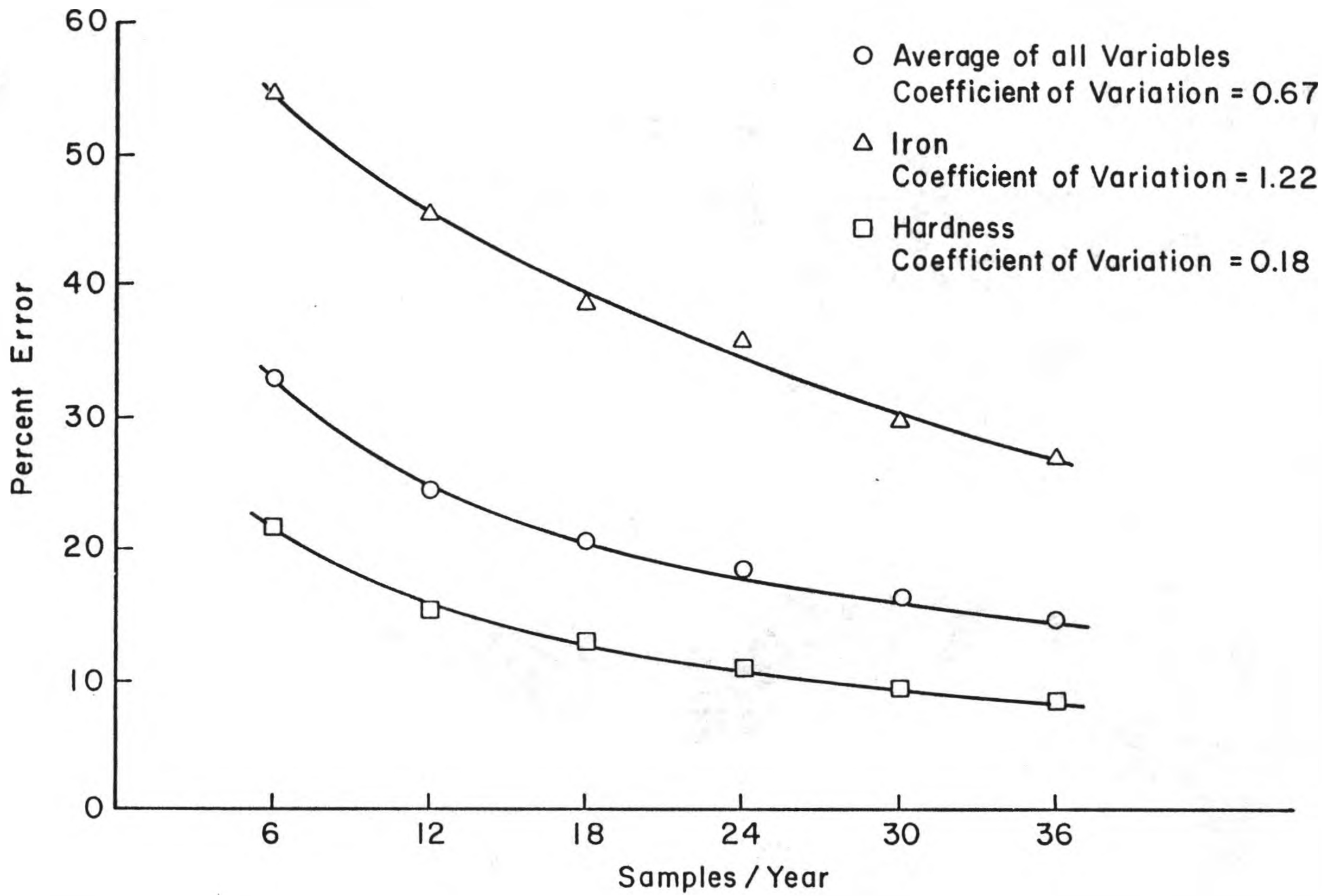

Figure B-2. Average absolute value of sample standard deviation error percentage.

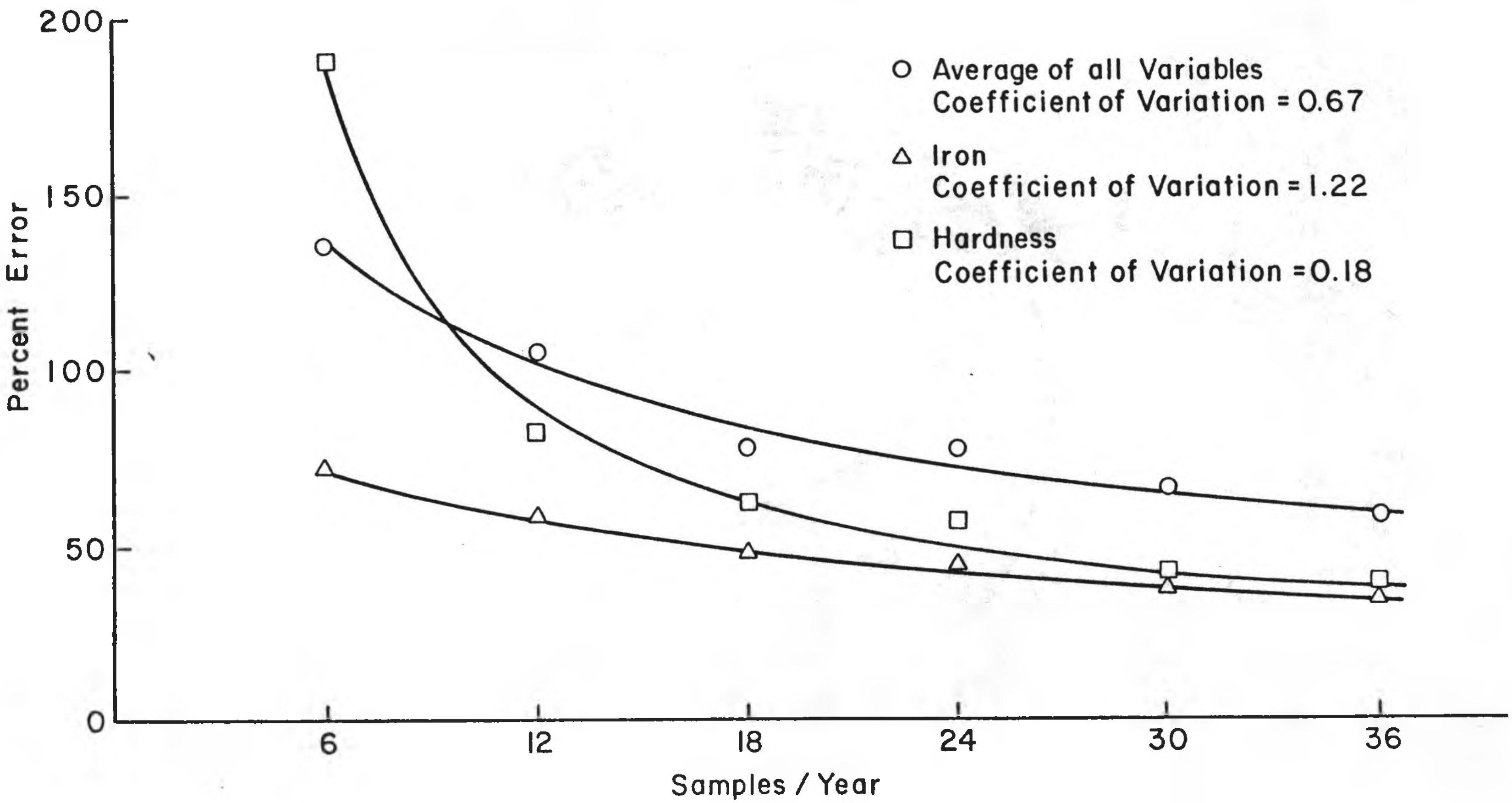

Figure B-3. Average absolute value of sample coefficient of skew error percentage.