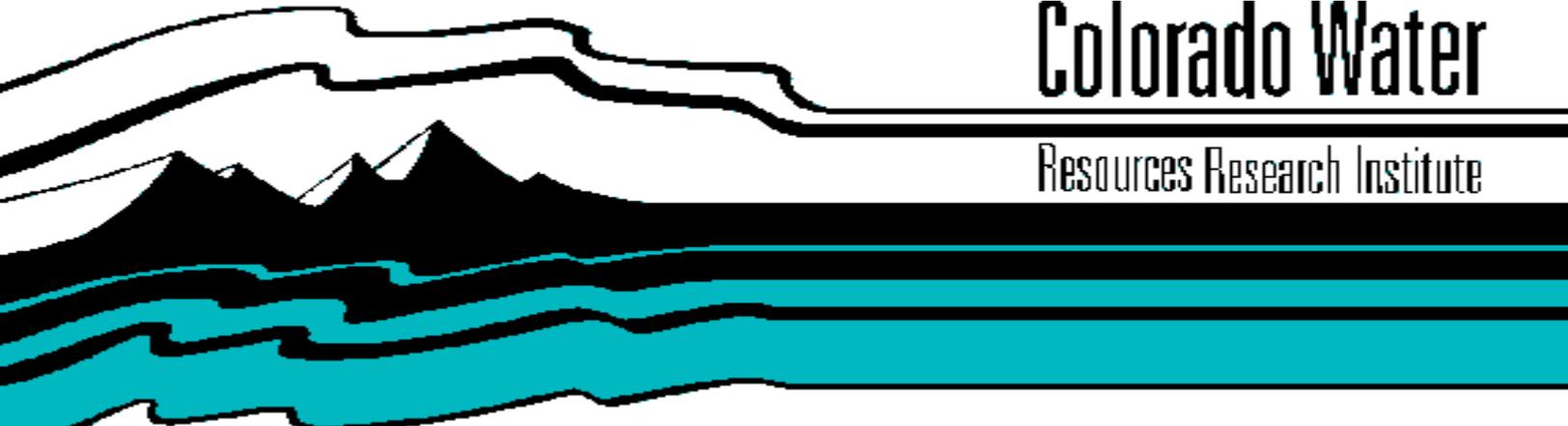


**MONITORING STRATEGIES FOR GROUNDWATER QUALITY
MANAGEMENT**

by

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Ward and T.G. Sanders**



Colorado Water

Resources Research Institute

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**Colorado
State
University**

**MONITORING STRATEGIES FOR
GROUNDWATER QUALITY MANAGEMENT**

by

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LIST OF PUBLICATIONS

Journal Articles Submitted

- (1) Loftis, J. C., J. Harris, and R. H. Montgomery. Detecting Changes in Ground Water Quality at Regulated Facilities. Submitted to Ground Water Monitoring Review, February, 1986

Anticipated Journal Articles

- (1) Statistical Characteristics of Ground Water Quality Random Variables
- (2) Statistical Methods for Characterizing Ground Water Quality Random Variables

ABSTRACT

A review of federal and state laws and regulations dealing with ground water quality monitoring revealed that the primary objective of monitoring is the detection of adverse changes in quality due to regulated facilities. State agencies are beginning to statistically analyze monitoring data for this purpose. Statistical procedures, which adequately address both the objective and the characteristics of the monitored variables are not yet implemented, however.

Analysis of case study data records indicated that ground water quality data may be seasonal, non-normally distributed, and serially correlated. Accurate characterization of particular variables is usually impossible, though, because of small sample sizes. Similarly, the statistical detection of changes of ground water quality is very difficult over a short time interval.

Keeping these limitations in mind, a "menu" of statistical procedures is recommended for characterizing ground water quality and for detecting changes. A "paired-well" approach is recommended for regulatory data analysis.

CHAPTER ONE

INTRODUCTION

Chemical contamination of ground water is perceived by many as the most serious environmental problem of the 1980's. Of particular concern is the contamination of public drinking water supplies by hazardous wastes, an issue brought to the forefront of public awareness by the Love Canal disaster.

Legislative response to the ground water quality problem produced two cornerstone federal laws, the Resource Conservation and Recovery Act (RCRA) in 1976 and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) in 1982. The former deals primarily with preventing and detecting ground water contamination. The latter deals primarily with cleanup of contaminated ground-water supplies.

These two laws, along with related pieces of federal and state legislation and regulations, either specify or imply a need for ground water quality monitoring to assist in regulating and managing the resource. With few exceptions, however, criteria for designing regulatory ground water quality monitoring programs are not specified. Neither are adequate guidelines available for analyzing monitoring data to provide information needed for regulatory purposes. Furthermore, the stochastic behavior of ground water quality random variables is, as yet, poorly understood. Therefore, a statistical approach to monitoring and data utilization is difficult.

The research reported herein is a first attempt to address comprehensively the statistical problems of ground water quality monitoring for regulatory purposes. The research concentrates on the stochastic behavior of ground water quality variables rather than on physical processes of ground water flow or contaminant transport. Furthermore, the research is limited to consideration of specific (point) sources of pollution, such as waste disposal ponds, and does not consider regional monitoring programs explicitly.

In a broader sense, the goal of this report is to provide a statistical foundation from which many issues of ground water quality monitoring can be addressed. Using this foundation, future researchers can hopefully begin to integrate a physical/chemical understanding of ground water quality with a stochastic understanding in order to more adequately address the issues of ground water quality management.

The report is organized as follows. Following this introduction, Chapters Two and Three discuss Federal and state requirements for ground water quality monitoring respectively. The most significant pieces of Federal legislation are discussed in Chapter Two, and Chapter Three presents the states' response, using case studies to describe current monitoring activities at the state level. The significant objectives of regulatory ground water quality monitoring are stated as conclusions of these chapters. Chapter Three also describes the data records contributed to the project by case study states.

Chapter Four contains a discussion of the stochastic behavior of ground water quality random variables. Some general conclusions are drawn based on results of previous research and analysis of the case study data records. These statements are intended as preliminary guidelines for selecting appropriate statistical procedures for use in regulatory monitoring.

Chapters Five and Six discuss statistical procedures in detail, providing specific suggestions on how data should be analyzed in light of the conclusions drawn in preceding chapters. Chapter Five deals with statistical procedures for characterizing ground water quality data, while Chapter Six deals with procedures for detecting changes in ground water quality at regulated facilities. Both chapters focus on the issue of limited length of record and/or small sample size in drawing statistically significant conclusions. Chapter Seven presents major conclusions of the work and recommendations for implementing a regulatory ground water quality monitoring program in a statistically sound manner.

CHAPTER TWO

FEDERAL REQUIREMENTS FOR MONITORING GROUND WATER QUALITY

I. Introduction

In 1981, Congress requested an assessment of the \$50 billion per year effort to restore and maintain water quality. Outwardly simple questions such as, "is the environment cleaner than it was 15 years ago?", went unanswered. The reason most often cited for this lack of knowledge is a lack of properly designed monitoring systems. Witnesses at a 1983 Congressional hearings on environmental monitoring have testified:

"unquestionably there is a most serious and pervading need for knowledge . . ."

". . . current monitoring does not adequately serve the important purposes of evaluating the progress of national environmental programs."

". . . we don't really know whether we are spending this (\$50 billion per year) wisely . . ."

(U.S. House of Representatives, 1983)

In order for the information provided by a monitoring system to be meaningful, the monitoring process must be linked to the nation's water quality goals in a rational manner (Sanders, et al., 1983). Indeed, the primary reason for monitoring is to assess progress toward these goals. Ward has stated "(monitoring) is the only connection between management and management's goals," and "any program of data collection must be tied to clearly stated goals." (Ward, McBride, 1986). This is illustrated in the monitoring system evaluation in Figure 1.1 (Ward, McBride, 1986). Step 1, evaluation of information expectations, provides the link between statutory and monitoring goals. Currently, most environmental monitoring is not the result of a planned intent to address national water quality goals, but rather a series of uncoordinated sampling and analysis events. Witnesses at Congressional hearings regarding hazardous waste management point to monitoring as a major weakness in ground water protection (U.S. House of Representatives, 1982).

- STEP 1 Evaluate Information Expectations**
- Water Quality Goals (maintain and improve)
 - Water Quality Problems
 - Management Goals and Strategy
 - Monitoring's Role in Management
 - Monitoring Goals (as statistical hypotheses)
- STEP 2 Establish Statistical Design Criteria**
- Statistically Characterize "Population" to be Sampled
 - . variation in quality
 - . seasonal impacts
 - . correlations present (independence)
 - . applicable probability distributions
 - From Many Statistical Tests, Select Most Appropriate (match test requirements to population characteristics)
- STEP 3 Design Monitoring Network**
- Where to Sample (from monitoring's role in management)
 - What to Measure (from water quality goals and problems)
 - How Frequently to Sample (from needs of statistical tests)
- STEP 4 Develop Operating Plans and Procedures**
- Sampling Routes
 - Field Sampling and Analysis Procedures
 - Sample Preservation and Transportation
 - Laboratory Analysis Procedures
 - Quality Control Procedures
 - Data Storage and Retrieval Hardware and Data Base Management Systems
 - Data Analysis Software
- STEP 5 Develop Information Reporting Procedures**
- Type of Format of Reports
 - Frequency of Report Publication
 - Distribution of Reports (information)
 - Evaluation of Reports Ability to Meet Initial Information Expectations.

Figure 2.1 Steps in the evaluation of a water quality monitoring system.
(Ward, McBride, 1986)

By reviewing the ground water monitoring implications of eight major environmental statutes, this chapter will illustrate some of the problems one can encounter when evaluating the information expectations of a ground water quality monitoring system. Ground water quality represents a special challenge to designers of monitoring systems. At the same time, ground water quality monitoring is relatively new to the regulatory scene and represents an opportunity to design a system which is capable of addressing the nation's ground water quality goals.

II. The Dilemma of Monitoring

The design and evaluation of a ground water quality monitoring system presents something of a dilemma. Water quality managers cannot interpret statutory goals without monitoring and technical information, nor can they efficiently obtain information without the tools and guidance provided by the statutes. When a problem, such as ground water contamination, has been identified but is poorly understood, water quality goals and expectations may be unrealistic. Questions which Congress must ask before setting realistic goals (how costly, who is affected, what are the most serious problems, etc.) cannot be answered without fairly extensive monitoring and technical assessments of water quality problems. A member of the House Subcommittee on Natural Resources, Agriculture Research and Environment has stated, ". . . there is no question that regulations will continue to be challenged in the courts . . . until we can guarantee that the regulations that are promulgated can be substantiated with good science . . . that is collected through the monitoring process." (U. S. House of Representatives, 1982)

The physical and chemical ground water environment is not understood well enough to design a monitoring system that will address all water quality goals. "Almost all activities of establishing a ground water monitoring program . . . are fraught with uncertainties, sources of error, and sources of well and sample contamination." (U.S. House of Representatives, 1981) "State and federal programs designed to address ground water quality problems are at a rather early stage of development compared to surface water programs, perhaps reflecting a far lower degree of knowledge of ground water quality dynamics." (U.S. House of Representatives, 1981) Some problems are related to the slow movement of ground water. Current monitoring may reflect events which occurred 10 to 20 years ago. (U.S. House of Representatives, 1981) In addition, there are both insufficient laboratory resources to monitor every conceivable contaminant and inadequate methods for setting standards for many substances which can be detected. (U.S. Environmental Protection Agency, 1984) This serves to emphasize that ground water quality information is expensive to obtain.

On the other hand, it may be much more expensive not to obtain ground water quality information. Even though quality changes in ground water occur slowly due to slow rates of pollutant movements, once contaminated, many aquifers are effectively permanently damaged.

III. Authority

The authority to create and interpret goals for the nations' environment is vested in the federal government. The relevant goals with respect to the nation's ground water quality can be found in federal law. While there is no single statute dealing exclusively with ground water, it is clear that the EPA, with the urging of Congress, could create a comprehensive ground-water quality policy based on existing law. (Tripp, Jaffe, 1979) A lawyer for the Environmental Defense Fund has stated, ". . . if all the existing pieces of legislation were adequately implemented and enforced and . . . you have a vigorous program for cleaning up existing abandoned sites, (CERCLA legislation) . . . that would be adequate (to protect ground water). EPA seems to feel they do not have authority under the Clean Water Act to review and establish standards of ground water. I happen to disagree." (U.S. House of Representatives, 1981)

There are many statutes dealing in some fashion with ground water quality. The most important (beginning with general laws and concluding with more specific laws) include the National Environmental Policy Act (NEPA), the Toxic Substances Control Act (TSCA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), the Resource Conservation and Recovery Act (RCRA), the Uranium Mill Tailings Radiation Control Act (UMTRCA), and the Surface Mining Control and Reclamation Act (SMCRA).

NEPA sets forth a broad environmental policy which has set the tone for subsequent legislation. TSCA controls virtually all aspects of man-made substances that have a potential to harm the environment. CERCLA grants authority to regulate releases of these substances to the environment. The CWA and SDWA are concerned with the presence of harmful substances in water (including ground water) and drinking water (including ground water). RCRA is concerned with managing solid and hazardous waste materials and preventing them from damaging the environment. UMTRCA and SMCRA deal with ground water pollution from the specific sources identified in their titles. For an overview of this body of legislation, the reader is referred to: Congress of the United States, Protecting the Nation's Groundwater from Contamination, 1984. More specific information and references are given in the following discussion.

IV. Ground Water Quality Monitoring Requirements of Specific Federal Laws

This section is a review of the monitoring goals which can be discerned from the eight major environmental laws listed above. Two types of goals are perceived: statutory and implied. Statutory monitoring goals are stated explicitly in the law in the form of specific requirements. Implied goals are those one may discern on interpretation of the statutory objectives or statutory goals.

A. National Environmental Policy Act

NEPA signals the start of serious legislation designed to protect the environment. It "establishes a national policy in environmental quality and directs federal agencies to use a systematic and interdisciplinary approach . . . to insure that environmental concerns are sufficiently considered." (Congress of the United States, 1984) NEPA has as goals:

- "to use all practicable means and measures . . . to create and maintain conditions under which man and nature can exist in productive harmony . . ."
- "assure . . . safe, healthful, productive, and aesthetically pleasing . . . surroundings . . ."
- "attain the widest range of beneficial uses . . . without degradation, risk to health or safety or other undesirable and unintended consequences" (Selected Environmental Law Statutes, 1983)

One finds with NEPA a characteristic repeated in other environmental statutes. While the goals are broad and extensive, the objectives and tools it provides are rather narrow. The objectives of NEPA are:

- to assess the impact of federally funded projects on the environment
- to create a council on environmental quality (CEQ) which will report on:
 - 1) the condition of the environment,
 - 2) trends in environmental quality,
 - 3) the adequacy of the environment to supply natural resources,
 - 4) environmental programs and activities of federal, state, and local governments.

These objectives do not fully encompass the goals of the statute. Logically, however, the EPA, in assessing its management goals and strategy, addresses only those objectives listed above. EPA does not, as a rule, deduce objectives from the goals of the law. "The absence of any clear Congressional mandate about and clear conceptual framework for addressing ground water quality is a major factor behind the difficulties which EPA has encountered in implementing regulatory programs affecting ground water under list of major environmental statutes." (U.S. House of Representatives, 1983) Until further Congressional direction, the executive branch will interpret the goals of NEPA to be:

- create environmental impact statements for federally funded projects,
- report, through the CEQ, on the status of the environment.

NEPA has no statutory monitoring goals. However, many interpret the second objective as making the CEQ responsible for managing the nation's environmental monitoring effect. Under "Duties and functions" NEPA states: "It shall be the duty and function of the Council (CEQ) . . . (U.S. House of Representatives, 1981) to gather timely and authoritative information concerning the conditions and trends in the quality of the environment . . . and submit to the President studies relating to such conditions and trends; . . . ", and to "review and appraise the programs and activities of the Federal Government." (Selected Environmental Law Statutes, 1983) Certainly, monitoring is justified on the basis of these responsibilities. The chairman of the CEQ has stated, "The CEQ will continue its role as catalyst in environmental monitoring." However, "CEQ does not, itself, carry out monitoring programs. . . it collects, integrates and interprets environmental data." (U.S. House of Representatives, 1981)

NEPA has had no tangible effect on ground water quality monitoring aside from its role of setting a tone for environmental policy. It does not provide water quality managers with specific objectives or tools that are relevant to ground water. Given further objectives and tools though, the potential for NEPA to have a tangible effect on environmental management is significant.

B. Toxic Substances Control Act

The goal of the Toxic Substances Control Act (TSCA) is to protect human health and the environment from toxic substances. TSCA provides authority to regulate the manufacture, processing, distribution, use, and disposal of substances which pose an "unreasonable risk" to human health and the environment. Objectives of the law include:

- to develop data with respect to the effects of chemical substances and mixtures on health and the environment,
- to establish the authority to regulate substances which are found to present such a risk,
- To establish the authority to regulate, specifically, PCB's.

Substances which present an unreasonable threat to ground water can be regulated throughout their existence.

TSCA itself has no specific monitoring requirements. However, the objectives cannot be fulfilled without information about the behavior of toxic substances in the environment. The development of this type of information relative to any particular substance is the responsibility of the manufacturer. As a result, the ability and incentive to conduct such real world monitoring has been limited to laboratory or literature studies.

EPA regulations based on TSCA require ground water sampling at all disposal sites that receive PCBs. No other substances (to date) require monitoring. Each site must have at least three wells that are to be sampled for PCBs, pH, specific conductance and chlorinated organics prior to the introduction of wastes on the site. Further reporting is not required. Additional monitoring may be required if there is evidence of contamination by any toxic substance.

C. Comprehensive Environmental Response Cleanup and Liability Act

The Comprehensive Environmental Response Cleanup and Liability Act (CERCLA), popularly known as Superfund, deals with releases of hazardous substances into the environment. The goal of CERCLA is to protect human health and welfare and the environment from such releases. Statutory objectives include:

- designate hazardous substances and amounts,
- provide authority and mechanisms for responding to releases,
- provide authority to collect money to finance responses,
- set civil and criminal penalties for failure to report or respond to releases,
- establish responsibility for releases.

Of all federal environmental laws, CERCLA has perhaps the greatest potential for protecting ground water. It requires EPA to set standards and force those responsible to clean up at their own expense. The only allowable defenses to releases are acts of God, acts of war, or

acts of a third party only if the defendant establishes by a "preponderance of evidence" that he/she exercised due care and took precautions against foreseeable acts or omissions of the third party. This is very strong language, and the allowable penalties are quite severe.

The statutory objectives of CERCLA could be interpreted to include virtually all sources of ground water pollution. (Exceptions are made for permitted releases, such as those under the NPDES program.) While the tone of the law is directed at what may be regarded as accidental releases, prevention is urged by the severity of penalties.

Monitoring is not specifically required by CERCLA. However, the statutory objectives imply a need for information concerning the hazard posed by a "release" of a hazardous substance. Regulations require ground water monitoring at abandoned hazardous waste dumps. Monitoring at other sites (spills, leaking storage tanks, etc.) is implied. The EPA has not thus far written any regulations for these situations.

D. Clean Water Act

The major goal of the Clean Water Act (PL92-500, the Federal Water Pollution Control Act Amendments of 1972) is to "restore and maintain the . . . integrity of the nation's water." Objectives pertinent to ground water include:

- regulate point sources of pollutants,
- develop water quality criteria (including ground water),
- provide basin-wide water quality planning,
- provide area-wide water quality planning,
- prohibit discharges of toxic pollutants in toxic amounts.

The "nation's waters" clearly include ground water (Tripp, Jaffe, 1979). However, many of the tools and funding in the law are for control of point source discharges to surface water. Tripp (Tripp, Jaffe, 1979) writes, ". . . although section 208 (areawide planning) provides some opportunity for comprehensive protection planning, without support from the Act's other provisions, it is simply inadequate as an overall solution." Subsequently, "as presently interpreted the CWA has limited value for controlling ground water pollution." "Cramped interpretation," not the law itself, is the cause of limited utility of the CWA to protect ground water quality.

The CWA, in Section 104(a) (Groundwater Contamination, 1984), required EPA in cooperation with state, local and other federal agencies to "establish, equip, and maintain a water quality surveillance system for the purpose of monitoring the quality of the navigable

waters and ground waters . . ." (42 USC 1254). EPA has not often used this authority. Only surface water and ground water beneath sites for land application of wastewater are monitored thus far.

The U.S. Geological Survey (USGS) has monitored a few inorganic constituents to characterize certain aquifers. USGS recently began a Regional Aquifer-System Analysis (RASA) program, a series of studies to provide information on the most important regional aquifers (U.S. Geological Survey, 1984). The studies will identify such things as regional flow directions, general water quality and regional use patterns.

E. Resource Conservation and Recovery Act

In contrast to the general legislation discussed thus far, RCRA addresses a particular threat to ground water quality. The goal of RCRA is to protect human health and the environment from poor solid and hazardous waste management practices. Objectives of the law include:

- establishing regulations concerning hazardous waste management,
- providing solid waste management guidelines to the states,
- providing the authority to regulate the disposal of solid and hazardous wastes.

Congress defines disposal to include practices which could affect ground water. RCRA also requires state interim programs for hazardous waste management to be "substantially equivalent" (Selected Environmental Law Statutes, 1983) to the federal program. This is stronger language than found in other federal environmental laws, which allow equivalent or more stringent programs. A comparison of RCRA and CERCLA is provided in Congress of the United States, "Groundwater Protection Standard for Hazardous Waste Land Disposal Facilities" (1984).

RCRA provides the authority to require monitoring at hazardous waste management facilities, and has as a monitoring objective to "ascertain the nature and extent of" the hazard to ground water posed by a release or the presence of hazardous wastes. (Selected Environmental Law Statutes, 1983) Implied monitoring goals include the monitoring of ground water at all sites where hazardous wastes are disposed. This would include sites used by small generators and households, which are not exempt under RCRA regulations.

Implied monitoring objectives include obtaining any information that can be used to assess the impact or potential impact of a

hazardous waste management facility. This might include background water quality, detection of leaks and determining hazardous waste transport in ground water. Current regulations require monitoring only at what EPA has defined as hazardous waste management facilities. This monitoring is limited to the goal of detecting a pollution event (leak). Once a leak is detected, other types of monitoring can be required.

Regulations promulgated under authority of RCRA are by far the most explicit with respect to ground water monitoring. The act addresses the disposal of both hazardous wastes and municipal solid waste. Regulations 40 CFR 265 apply to interim status hazardous waste storage and disposal facilities. Permitted facilities regulations are contained in 40 CFR 264.

The regulations require a statistical test for comparing data. A specific test, the Student's t-test, and a 0.01 significance level are required at interim facilities. Cochran's Approximation to the Behrens-Fisher Student's t-test at 0.05 significance level (or an equivalent test) is to be used at permitted facilities. These regulations are unique in requiring a statistical test. There are some serious problems with the specific regulations, for example, assuming all the measured variables behave similarly so that one test is sufficient; however, the requirements demonstrate that EPA is aware of the statistical nature of ground water quality monitoring.

Requirements for interim facilities are much more explicit than those for permitted facilities, because many of the details cannot be supplied in the permit, and site-specific conditions cannot be taken into account. The interim status regulations require ground water monitoring of the uppermost aquifer underlying the hazardous waste disposal site. The monitoring system must include at least one upgradient and three downgradient wells, located to insure any statistically significant amounts of hazardous waste that enter the ground water will be detected. The owner or operator is required to develop a sampling and analysis plan that includes procedures for sample collection, preservation and shipping and for analytical procedures and chain of custody control. Background concentrations of drinking water parameters and four indicator variables must be determined by taking quarterly samples for one year in a monitoring well which is not affected by discharge from the facility. After the background values are determined, samples are to be taken semi-annually for the indicator variables and annually for the drinking water variables. The owner or operator of the facility is required to submit a plan for a more comprehensive monitoring system, to be implemented when a significant increase in a sampled variable is detected.

Three types of monitoring may be required at hazardous waste facilities which have received permits, detection, compliance and corrective action monitoring. Detection monitoring is similar to the monitoring required at interim facilities, with the monitored variables specified in the permit.

Compliance monitoring is required when an increase in a contaminant is detected in the ground water. If a high concentration of a substance which reasonably could be expected to occur in the waste stored at the facility is detected in determining the background ground water quality, then a compliance monitoring program may be required in the permit. Otherwise, compliance monitoring is begun as a response to an increase in a contaminant discovered in the detection monitoring program. Compliance monitoring programs are based on conditions at specific sites and are set primarily by individuals who write the permits. As a result, the application and effectiveness of compliance monitoring probably varies over a wide range.

Corrective action monitoring is required to characterize the effectiveness of any modifications to the facility or its operations that were instituted as a result of ground water contamination. The program must be at least as effective as the compliance monitoring program. No other criteria are given.

The Hazardous Waste Control and Enforcement Act of 1983 amends RCRA. It requires a study by EPA of the extent to which the guidelines and criteria under this act are adequate to protect human health and the environment from ground water contamination. The study shall include "a detailed assessment of the degree to which the criteria . . . regarding monitoring, prevention of contamination and remedial action are adequate to protect ground water." Following a report, to be submitted to Congress not later than 36 months after enactment of the amendments, EPA shall revise the guidelines and criteria to the extent necessary to insure that such guidelines and criteria are adequate.

F. Safe Drinking Water Act

The SDWA has a goal, the protection of human health from contaminated drinking water. Objectives of the law include:

- establishing of drinking water standards,
- identifying the presence and source of drinking water contaminants,
- establishing Underground Injection Control (UIC) operating standards,
- protecting sole source aquifers from federally funded projects.

The objectives of the law fall short of the goal. It has been said that the law should be renamed the "Polluted Drinking Water Supply Clean-Up Act" because the statutory objectives and the EPA focus is on clean-up rather than protection of drinking water sources (i.e., UIC and federal threats to sole source aquifers). (U.S. House of Representatives, 1983)

The law provides no funding to communities with polluted drinking water, nor does it force those responsible to remedy the situation. Consequently, it is claimed that most water utilities do not know the chemical quality of the water they provide. (U.S. House of Representatives, 1983)

At recent Congressional hearings a witness from the firm of Geraghty and Miller testified that, ". . . source oriented programs, such as UIC and RCRA, are not protecting ground water supplies." (U.S. House of Representatives, 1983) The EDF at these same hearings stated that, "The objective (of the SDWA) should be the maintenance, protection, and restoration of the quality of the country's present and future ground and surface drinking water supply sources." (U.S. House of Representatives, 1983) Some feel that this implies a non-degradation policy in certain situations.

The SDWA does take the important step of recognizing that recharge areas are relevant to the protection of ground water. However, what constitutes a recharge zone and the steps a community may take to protect such a zone are not defined.

Regulations affecting ground water have been promulgated under authority of the Safe Drinking Water Act only in the Underground Injection Control (UIC) program. Injection wells are divided into five classes based on the use of the well and the proximity of an "underground source of drinking water." For example, a Class I injection well is one that injects hazardous wastes beneath the lowermost formation containing, within 1/4 mile of the well bore, an underground source of drinking water (40 CFR 146.5[a]). The owner or operator of the well is required to notify the regulatory agency of the "type, number and location of wells within the area of review to be used to monitor any migration of fluids into and pressure in the underground source of drinking water, the parameters to be measured and the frequency of monitoring." (40 CFR 146.13[b]) (Congress of the United States, 1984) The regulations include all aquifers currently being used as drinking water sources and all aquifers containing less than 10,000 mg/l TDS, as underground sources of drinking water.

EPA has set drinking water standards under authority of the SDWA, but the standards apply at the tap where water is delivered to the

user. The standards have been applied to ground water in other regulations, for example, in hazardous waste facility regulations (40 CFR 265), but they were not applied as ground water standards under this act.

G. Uranium Mill Tailings Radiation Control Act

UMTRCA required regulations by EPA for inactive uranium mill tailings piles and by the Nuclear Regulatory Commission (NRC) for active sites. EPA's regulations are specific with respect to the information requirements, but flexible with respect to the procedures for supplying the information. Regulations require a hydrologic and geologic assessment at each site "to include a monitoring program sufficient to establish background ground water quality through one or more upgradient wells, and to identify the presence and movement of plumes associated with the tailings piles." (40 CFR 192.20[a]) (Congress of the United States, 1984) The location of any contaminants released from the tailings piles and the rate and direction of movement of contaminated ground water are to be assessed. Periodic reporting of specific constituents is not required.

NRC regulations for active uranium mills do not list specific requirements for network design. However, a list of the objectives of the monitoring program is given in 10 CFR 40, Appendix A. The objectives are:

1. to evaluate compliance with applicable standards and regulations,
2. to evaluate performance of control systems and procedures,
3. to evaluate environmental impacts of regulations, and
4. to detect potential long-term effects.

A design requirement is to prevent seepage that would deteriorate ground water supplies from current or potential uses.

The information from monitoring is used to evaluate both compliance with license requirements and the need for operational modifications.

H. Surface Mining Control and Reclamation Act

SMCRA regulations specify minimum ground water monitoring as part of the permit process. The regulations were written by the Office of Surface Mining Reclamation and Enforcement (OSMRE). A measure of seasonal quality and quantity of ground water with baseline information

on at least total dissolved solids or specific conductance corrected to 25°C, pH, total iron and total manganese are required. The permit application is to contain a ground water quality monitoring plan which includes the parameters to be monitored, sampling frequency and site locations. The plan must also describe how the data may be used to determine the impacts of the operation on the hydrologic balance. Data are to be reported every three months.

V. Monitoring Roles

Although the listed regulations seem long and complex, there are relatively few objectives for the monitoring programs. The CWA requires surveillance of the nation's ground water, but all other legislation is directed at specific sites or substances.

Regulations from four of the laws require monitoring to determine background or baseline water quality data. They are RCRA, SMCRA, TSCA and UMTRCA. None of the regulations require more than one year of quarterly samples as a minimum. In RCRA and SMCRA, the background values are used to determine standards included in permits as well as to determine which constituents require monitoring at the facility. UMTRCA background data requirements are very general. The intent of requiring the data appears to be to produce a standard against which to determine increased radioactivity, but nothing is explicitly stated regarding the use of the data. Similarly, no explicit statement appears in the TSCA regulations regarding use of the required background data.

The permit programs, RCRA, SMCRA, UIC and UMTRCA, require monitoring to determine compliance with ground water standards. Since the only ground water standards now in place are those set for drinking water, either those standards are applied or the background constituent level is set as a standard. In all the regulations, non-compliance can lead to operational changes or corrective action.

Monitoring to detect ground water contamination is an objective of monitoring at non-permitted facilities, RCRA interim facilities and inactive uranium mill tailings piles. This objective is similar to the one listed above, determination of permit compliance, but the objective criteria of standards are missing. In the case of RCRA, the background water quality is used as the standard. For uranium mill tailings piles, determination of contamination is left to the discretion of the owner of the tailings pile.

The final objective of ground water monitoring is to characterize the effectiveness of corrective action. Superfund is the most obvious

use of this objective, but RCRA, SMCRA, UMTRCA and UIC also contain provisions that require corrective action and use information from monitoring to assess the need for further action or a return to initial operating procedures. A successive corrective action is one that returns the concentration of the contaminant to levels within the standard.

An instructive comparison can be made between surface water and ground water monitoring. In 40 CFR 35, Appendix A, EPA lists the objectives that any state should have for its surface water monitoring program. The objectives are to provide data necessary to determine permit compliance, to develop and maintain an understanding of water quality to support pollution control activities, to report on quality and its causes and effects, and to assess the effectiveness of the state's pollution control program.

Only the first objective, provision of data for the determination of permit compliance, can be applied directly to ground water monitoring. There are no ground water pollution control activities, except design criteria for waste disposal sites, that could be supported by monitoring data. There are no requirements for a state, or any other group, to report on general ground water quality, and no provisions to determine cause and effect relationships. The fourth objective would apply only in the sense that the effectiveness of state or federal pollution control programs is reflected in permit compliance.

The requirements for ground water monitoring are very specific, problem-oriented programs. They are directed toward self-monitoring at high-risk, generally privately-owned sites. This implies a reluctance on the part of EPA and Congress to monitor overall ground water quality. EPA has not written regulations under the authority of the CWA, and Congress has not required that they do so.

Based on these observations, EPA and Congress regard the early detection of contamination as the primary purpose of ground water monitoring. A secondary purpose is the characterization of corrective action. Determination of overall ground water quality is not an objective.

VI. Summary

The lack of an explicitly stated framework of ground water quality management at the federal level forces monitoring network designers to induce a general role for ground water monitoring from specific documents issued at the federal level. This report surveyed federal

legislation and EPA regulations to determine the role of the required (both statutory and implied) monitoring. Four major objectives were identified:

1. determination of background ground water quality,
2. determination of permit compliance,
3. detection of ground water contamination, and
4. characterization of the effectiveness of corrective action.

The overall purposes of monitoring in ground water management appears to be the early detection of contamination and the characterization of corrective action applied to contaminated aquifers.

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CHAPTER THREE

STATE REGULATIONS AND MONITORING ACTIVITIES

I. Introduction

Groundwater quality protection or regulation efforts by individual states have fallen into three general categories or approaches. This multi-level approach by the states has enabled each one to regulate ground water resources with the idea of making the most beneficial use of the resource while protecting its quality as well.

The three categories of ground water protection mentioned above may be defined as differential protection, limited degradation, and non-degradation. Differential protection calls for different levels of ground water quality protection based on current ground water uses, characteristics, and future or anticipated uses. Limited degradation allows for degradation up to a given standard, attempting to minimize degradation. Non-degradation, the most protective policy, specifies the protection of ground water at its existing quality.

In a survey of 14 state programs, Henderson et al. (1984) found that all, except Wisconsin, have opted for a ground water protection policy of either limited degradation, differential protection, or some combination of the three categories mentioned above. This approach allows the states a great deal of flexibility in their approach to ground water quality protection in that aquifers which are currently clean could be degraded to some extent if other conditions dictated this course of action.

Wisconsin has chosen to approach ground water quality from a unique position (Henderson et al., 1984). Aside from allowing no degradation of present aquifer quality, it has implemented a two-tiered approach to ground water quality standards. Two standards must be set for each substance which is currently present in or might be expected to contaminate ground water. These two standards are the "preventive action limit" or PAL and the "enforcement standard."

The enforcement standard is the same as that normally specified by a governmental agency. The "preventive action limit" (PAL) is specified as 10%, 20%, or 50% of the enforcement standard, depending on the health-related characteristics of the particular substance. The PAL has two major purposes:

1. it is the standard used in design codes and specified management practices, thus requiring more stringent designs, and
2. it is a "trigger" to examine the site for remedial action before an actual violation has taken place.

This trigger aspect of the PAL is unique in that it causes the regulatory agency and/or discharger involved to examine the possibility of taking remedial action before an actual violation of the enforcement standards has taken place.

II. Overview of Case Study States

Case study states were selected to provide specific examples of ground water quality management and monitoring strategies which are currently being implemented at the state level. The primary case study states were New York, Illinois, Colorado, Wyoming and California. Information from these states was obtained through personal visits, mail and phone conversation. Each of these states contributed ground water quality data to the project. Additionally, the state of Oklahoma was contacted by phone for information on current monitoring activities.

Before moving on to an examination of the specific regulations and agencies dealing with ground water quality within each case study state, a few general comments common to most of the case study states are in order.

Groundwater regulation in most of the states is generally handled in a loosely organized fashion by several agencies which may be interconnected or independent. Due in large part to a lack of manpower and funds, most states thoroughly examine only the monitoring data of their most hazardous sites. Those sites which are not considered very hazardous, such as sanitary landfills, are usually examined only on a complaint basis. The state agencies charged with ground water regulation are aware of their own limitations in this regard but are forced by resource limitations to focus their attention on sites that represent the greatest danger to the public health.

Groundwater laws vary considerably from state to state. In Illinois, a single law governing hazardous waste disposal and emphasizing ground and surface water protection was passed in 1984. This law organized ground water protection and regulation under a single agency and removed much of the confusion over who regulates what site.

In New York and Wyoming, a single law has been passed to deal with almost all environmental issues, including ground water protection. This means that, although ground water protection is now handled by a single agency, the regulation of different sites can become non-uniform because there are several divisions within the agency regulating similar sites in different ways.

California and Colorado have taken the approach that laws already in existence can be applied to ground water protection and that the agencies currently administering those laws can enforce them with respect to ground water also. This approach results in confusion as to which agency regulates a particular site and confusion on the part of persons applying for a discharge permit as to whom applications should be directed.

If one views the process of ground water quality regulation as an evolving one--which it is--then it can be said that Illinois has the most fully evolved regulations and California and Colorado the least evolved. This does not imply that ground water quality regulation is the best in Illinois. Overall performance of regulatory programs is determined by variety of factors, such as funding and manpower available. It does imply that the regulations in Illinois are the easiest to understand and, hopefully, to follow by dischargers. California is currently studying the idea of creating a single agency to handle ground water regulation at hazardous sites to reduce confusion among both state personnel and dischargers.

Although most states do have a large ground water monitoring data base, the data may be of little use in a statistical study. In the five states examined in this study, there were only a very few sites with more than 20 samples per well for any number of wells sampling the same aquifer other than drinking water wells. Most sites had 6 to 15 samples per well for a total of 3 or 4 wells sampling the same aquifer. This was true even of sites which have been sampled since the early 1970's and is due to the haphazard approach to (or lack of) sampling by most states prior to about 1977 to 1980. At that time, the states realized that the Federal Government was serious about implementing RCRA. Currently, most sites are sampled only semi-annually (or quarterly at most). Thus, a "statistically adequate" number of data points will not be available for most sites until the late 1980's or early 1990's. More quantitative discussion of the limitations of small sample sizes appears in later chapters of this report.

III. New York

New York has taken a rather unique approach to environmental protection (Roberts, 1985; Hammond, 1985). It has chosen to combine the significant federal environmental laws enacted since 1970 into a single law, the Environmental Conservation Law of the State of New York. Other states have combined several pieces of federal water protection or cleanup legislation into a single act. Going still further, New York has combined federal acts as divergent as the Clean Air Act, the Clean Water Act, the Resource Conservation and Recovery Act (RCRA), the Marine Protection Research and Sanctuary Act, and the Comprehensive Environmental Response, Compensation and Liability Act (Superfund). Only those parts of the New York law dealing with ground water quality will be discussed here.

The Environmental Conservation Law created the Department of Environmental Conservation to administer the provisions of the Law. Within the Department is the Division of Solid and Hazardous Waste, which has the primary responsibility for enforcing the ground water quality sections of the Law. The various County Health Departments are also quite active in ground water quality monitoring and regulation at present, but the state seems to be gradually assuming more responsibility in this area.

The Division of Solid and Hazardous Waste has the responsibility for permitting and reviewing monitoring data submitted by the owners or operators of all solid and hazardous waste sites within the state of New York. These sites include active and inactive municipal landfills, mine waste piles, and sites at which hazardous chemical and radioactive wastes are stored for temporary or permanent disposal. It should be noted here that the State of New York has, through the previously mentioned Law, taken over the enforcement of RCRA from the U.S. EPA, thus the permitting, monitoring and "cradle to grave" tracking requirements of the Division (including the appropriate statistical tests for compliance) regarding hazardous wastes and waste sites are consistent with those required in RCRA.

The County Health Departments, at present, monitor ground water quality at municipal drinking water wells and at certain other sites (usually municipal landfills) which have the potential to affect ground water quality. The monitoring activities of County Health Departments are especially vigorous on Long Island where most of the aquifers are designated as "sole source" aquifers that supply drinking water to millions of people.

An interesting point to note here is that, in the past, the County Health Departments have been much more active in ground water monitoring than the State. Various State personnel have acknowledged that the

Counties (especially on Long Island) have data records of the size required for statistical analysis, while the State does not have data records of the required size at present. Cortland County in western New York has even developed a model of the ground water flow in the uppermost aquifer which underlies most of the county. The purpose of the model is to help determine the placement of monitoring wells to detect ground water contamination before it reaches municipal drinking water wells.

It is currently unclear what the working relationship between the County Health Departments and the Division of Solid and Hazardous Waste will finally be. It is anticipated that the Division will eventually assume most of the monitoring and enforcement responsibility at landfills within the state except on Long Island. The current attitude seems to be that, because of the large number of people affected, monitoring and enforcement on Long Island should stay on the county level.

The Division of Solid and Hazardous Waste uses logical approach to data analysis. All the monitoring data they receive is given at least a cursory visual examination to detect what appear to be any major pollution problems. Data sets which appear to show a problem are then analyzed by the statistical methods set forth in RCRA or another appropriate method to determine whether a problem actually exists before any enforcement action is taken. Data sets which do not appear to show a problem are analyzed by the methods stated above after the problem data sets have all been acted upon.

IV. Illinois

Groundwater quality regulation in Illinois is covered by a single comprehensive act, the Illinois Environmental Protection Act. This Act complies with all of the major requirements of the following federal acts: the Clean Water Act; the Safe Drinking Water Act; the Resource Conservation and Recovery Act (RCRA); and the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund). The Illinois Environmental Protection Act also created three bodies to administer the provisions of the Act: the State Pollution Control Board, the State Hazardous Waste Advisory Council, and the Illinois Environmental Protection Agency (Neinker, 1984).

The State Pollution Control Board is the policy making and judiciary body designated by the Act. The Board has the responsibility for issuing standards for water quality, including ground water, and adopting rules and regulations to regulate water quality. However, the standards issued by the Board must be approved by the U.S. EPA before they are implemented. The Board also has the responsibility of

conducting hearings on the violation of regulations or standards by a permit holder and of hearing appeals on the denial of permits by the Illinois Environmental Protection Agency.

The State Hazardous Waste Advisory Council is the body charged with the review of hazardous waste disposal technology. The three specific duties of the Council are:

1. to review the implementation of the procedures for the siting of new hazardous waste disposal facilities,
2. to review alternative ways to treat hazardous wastes and promote their use, and
3. to review existing State and Federal hazardous waste laws and report annually to the Governor and General Assembly with suggestions of administrative and legislative changes necessary to protect the public from harm by hazardous wastes.

The Illinois Environmental Protection Agency (IEPA) is the regulatory body designated by the Act. IEPA is responsible for issuing discharge permits for both surface and subsurface water bodies and enforcing permit compliance in accordance with the National Pollution Discharge Elimination System (NPDES) specified by the Clean Water Act and the Underground Injection Control (UIC) program specified by the Safe Drinking Water Act. IEPA fulfills its enforcement responsibilities by requiring monitoring of both ground and surface water at permit sites in accordance with RCRA and by unannounced site inspections. IEPA also has the statutory authority to commence corrective or preventive action at a site if it deems such action necessary to protect the public health in accordance with Superfund.

The Illinois Environmental Protection Act, in addition to the above bodies, created two funds, the Hazardous Waste Fund and the Hazardous Waste Research Fund, that are funded by a fee imposed on the disposal of hazardous wastes within the state. The Hazardous Waste Fund received 80% of the fee money for use in the cleanup of Illinois Superfund sites. The Hazardous Waste Research Fund receives 12.5% of the fee money to fund research and development on ways to recycle, detoxify, reduce the volume of, or reduce the hazardous properties of hazardous wastes in Illinois. The remaining 7.5% of the fee money is used for administering the fee collection procedure.

There are two state agencies in Illinois which are currently involved in ground water quality monitoring programs; the Illinois Environmental Protection Agency and the Illinois State Water Survey. The role each of these agencies play in ground water quality monitoring is discussed below.

The Illinois Environmental Protection Agency is responsible for monitoring the ground water quality at a variety of site types. IEPA receives monitoring data on hazardous waste sites, non-hazardous waste sites, deep well injection sites, and surface mining sites. The majority of IEPA's time and resources go into the monitoring of hazardous waste sites because these sites have the greatest potential for environmental damage. As of late May 1984, IEPA was in the process of computerizing its hazardous waste site monitoring data for use with the Statistical Analysis System data analysis package, prior to that time, all data analysis was done by a linear regression analysis for trends. The monitoring data from other types of sites (i.e. surface coal mining sites and sanitary landfills) is examined only on a complaint basis because of a lack of resources. Although IEPA routinely receives ground water monitoring data from 80 to 120 surface coal mining sites and approximately 250 non-hazardous sites, these data are filed and never examined unless someone complains about a particular site.

The Illinois Environmental Protection Agency has recently completed a survey of the hazardous waste sites within the state. IEPA has identified 38 hazardous waste sites, 27 of which require remedial action (11 are Superfund sites). IEPA has also compiled a list of the types and quantities of new wastes being generated within the state as part of the "cradle to grave" tracking system required of hazardous wastes by RCRA. At present, IEPA has interim authorization for RCRA from U.S. EPA.

The Illinois State Water Survey is in the process of designing a state-wide ground water monitoring network. ISWS's monitoring network is being designed with an emphasis on ground water quality and water levels in drinking water supplies. ISWS uses the federal Safe Drinking Water Act as the authority to set up its monitoring network.

V. Colorado

Groundwater quality regulation in Colorado is dispersed among several state agencies (Looft, 1982). The Department of Health is the agency primarily concerned with ground water quality, but the Department of Natural Resources and the State Engineer's Office also have some responsibility for ground water quality. An examination of the role each of these agencies plays in ground water quality regulation should help illustrate the patchwork nature of ground water protection in Colorado.

The Colorado Department of Health currently has four agencies with responsibility for ground water quality protection. These agencies are

the State Board of Health, the Waste Management Division, the Water Quality Control Commission, and the Water Quality Control Division.

The State Board of Health is primarily a policy body with broad authority regarding public health and safety. The Board thus has an indirect responsibility for almost all ground water quality within Colorado because of the ground water quality impacts on public health. The Board also has specific authority under the Colorado Management and Disposition of Solid and Hazardous Waste Act (enacted pursuant to the federal Resource Conservation and Recovery Act, RCRA) to promulgate rules and regulations establishing the design and operation of hazardous waste disposal sites.

The Colorado Management and Disposal of Solid and Hazardous Waste Act gave the Waste Management Division the authority to regulate hazardous waste generation, treatment, storage, and disposal. The Act requires that hazardous wastes be tracked by the "cradle to grave" system specified in RCRA. The Act also created the Committee on Hazardous Waste to formulate rules and regulations to protect the public health and environment from the effects of hazardous wastes. The rules and regulations formulated by the Committee must be approved by the Board of Health and may not be more stringent than those promulgated by EPA pursuant to RCRA.

The Colorado Water Quality Control Commission is a policy body with authority to develop and maintain a program for the prevention, control, and abatement of water pollution in the State. The Colorado Water Quality Control Act of 1973, as amended (enacted because of the federal Clean Water Act), required the Commission to set up a classification system for all state waters and promulgate water quality control standards and regulations to be used in developing and enforcing the State's water classification system. The Commission has developed a classification system for the State's surface waters and has received the recommendations from a Task Force it established to classify the State's groundwaters, but has not addressed the Task Force's recommendations.

The Colorado Water Quality Control Division is the enforcement arm of the Water Quality Control Commission. The Division is responsible for administering and enforcing the water quality control standards and regulations promulgated by the Commission. The Division has developed a comprehensive ground water protection program that should receive final approval from the Commission in the Spring of 1985. A brief review of the program is presented below.

The basis of the program is the concept of protecting ground water for a designated use. The concept was implemented by defining three

classes of ground water use based on Total Dissolved Solids (TDS) concentrations in parts per million (ppm). The three classes are: suitable for most uses; less suitable, but acceptable for most uses; and unsuitable for most uses. TDS concentrations are to be used as a screening mechanism for a particular site. The final classification of a site will be established by 1) defining what individual constituents must be limited or prohibited from that site to preserve its present and future beneficial uses and 2) examining the potential use, geologic conditions, and other appropriate factors affecting that site.

Plans for monitoring and enforcement are in the developmental stage. However, it is expected that the State will review monitoring results supplied by the site operator to determine if the use classification of the site is being maintained.

Within the Department of Natural Resources, the primary agencies responsible for ground water quality protection are the Oil and Gas Conservation Commission and the Mined Land Reclamation Board. Both agencies have the statutory and regulatory authority to promulgate environmental standards, including those pertaining to ground water quality protection.

The Colorado Oil and Gas Conservation Commission has the authority to regulate oil, gas, and geothermal well drilling operations within the State. The Commission has the responsibility to protect the ground water quality from contamination which may occur as a result of faulty drilling procedures for oil, natural gas, and geothermal wells. The Commission must examine all such wells in the State each calendar year to insure that they are drilled, operated, maintained, and abandoned in a safe manner. The Commission was also given the responsibility, under Colorado Senate Bill #10, of assuming control over a portion of the Underground Injection Control Program as provided by under the federal Safe Drinking Water Act.

The Colorado Mined Land Reclamation Board is required to develop, promulgate, and enforce standards to protect the State's land and water resources during and after open mining processes. The Colorado Surface Coal Mining Reclamation Act of 1979 (enacted pursuant to the federal Surface Mining Control and Reclamation Act) requires that the Board issue a permit before any surface mining operation may begin. The state's Act is exceptionally thorough in its treatment of ground water quality protection in that it specifies acceptable mining practices, requires permittees to maintain records of their mining operations, and requires regular monitoring of the ground and surface water quality (including background data) both on and off site. The Board may also designate areas unsuitable for surface mining, including areas where surface mining would adversely affect aquifers or aquifer recharge zones.

The Colorado Division of Water Resources in the Office of the State Engineer is primarily concerned with the administration of water rights in Colorado. The Division is concerned with ground water quality because its investigative section provides data and ground water expertise to other state agencies who are actively engaged in ground water quality regulation. The Division also provides staff and support for the Board of Examiners of Water Well and Pump Installation Contractors which is charged with the regulation of the water well construction industry in Colorado.

VI. Wyoming

The legal and regulatory basis for monitoring in the State of Wyoming is fairly complex (Ogle, 1984; Revall, 1985). The actual authority for monitoring requirements imposed by the state through the permit process stems from a single state act, The Wyoming Environmental Quality Act and its associated Rules and Regulations. The Act and Rules and Regulations, contained in several chapters, are of course much influenced by federal legislation and regulation; the major pieces of federal legislation involved are, the Clean Water Act, the Surface Mining Control and Reclamation Act, the Solid Waste Disposal Act, and the Resource Conservation and Recovery Act.

Three state agencies within the Department of Environmental Quality are actively involved in ground water quality monitoring: the Solid Waste Division, the Water Quality Division, and the Land Quality Division. The monitoring activities of these three divisions are described below.

The Solid Waste Division deals with permitting and control of land disposal sites which are not designated as hazardous waste sites. A plan for water quality monitoring of wells around the sites is a necessary part of most permit applications. An effort is made to require "background" water quality data from which future changes can be determined. This requires monitoring before disposal has begun or monitoring of a representative, but unaffected well. In practice, it is often difficult to meet either of these conditions.

The Water Quality Division is concerned with permitting and control of land disposal of liquid wastes, of lagoon-type treatment facilities, and of hazardous waste disposal. Although most permit applications do not fall under the provisions of RCRA, ground water quality monitoring is routinely required in permits. Here again, an attempt is made to secure upgradient or background data for comparison with downgradient data which would presumably be affected by the facility. For non-RCRA type sites, the period for background monitoring may be

very short, providing for only one or two samples, and placing an unaffected well is often difficult. Therefore, Division personnel are often unable to obtain an adequate picture of background conditions.

The Land Quality Division has the largest ground water data base of the three divisions. As a part of the permit process for mining applications, ground water monitoring is required for at least one year to establish background conditions. Monitoring is continued throughout the mining and reclamation period. A very large data base, therefore, exists in mine permit applications and annual reports.

Several important observations should be noted regarding the visits with Wyoming agency personnel. First is an acute awareness of the importance of ground water quality monitoring in the regulatory process. Even though RCRA directly impacts an almost insignificant fraction of their current monitoring activities, agency personnel are aware that this legislation is the first to specify the details of a monitoring program and a statistical analysis procedure. It, therefore, serves as a model for similar programs.

Agency personnel are also aware that the provisions of RCRA, including obtaining adequate background data and applying statistical tests for changes, are easier to legislate than to accomplish in practice. The Land Quality Division has begun to look at some possible methods of statistical analysis, including the t-test, but has been stymied by the usual problems of small sample sizes and non-normal distributions.

VII. California

Several state agencies in California have responsibility for the protection of ground water quality on either a state or regional level (Fischer, 1984; Souther, 1984; Wolfe, 1985). On the state level, the State Water Resources Control Board and the Department of Health Services share the responsibility for ground water quality protection, although most of the responsibility falls to the Department of Health Services. The Regional Water Quality Control Boards and the County Health Departments have the ground water quality protection responsibility on a regional level.

The legal authority for water quality regulation in California stems from a single act, the Porter-Cologne Water Quality Control Act. This act, with its associated rules and regulations, is fairly complex in that it addresses the major points of several pieces of federal legislation including the Clean Water Act, the Safe Drinking Water Act, the Resource Conservation and Recovery Act (RCRA), and the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund).

Under the Porter-Cologne Act, the State Water Resources Control Board has over-all responsibility for the regulation of both water quality and quantity (water rights) in California. The Board has two divisions to carry out its duties, the Division of Water Resources and the Division of Water Quality. The Division of Water Resources has responsibility for the administration of water rights as well as the protection of existing ground water quality state-wide. The Division of Water Quality has the responsibility of regulating point source discharge, by the permit process, to both the surface and groundwaters of the state to protect water quality.

The Department of Health Services has the authority to require monitoring and to oversee any corrective action necessary to stop ground water contamination at solid waste dumps (landfills) and at sites which could harm human health within the State. At present, the Department has primary monitoring and corrective action responsibility for both RCRA and Superfund sites. The Department is also responsible for the protection of drinking water supplies through discharge permits that are issued in cooperation with the Division of Water Quality. Additionally, the Department works with and/or under the State Water Resources Control Board to clean up and monitor both ground and surface water sites that are, or have the potential to be, major water quality problem sites within the state.

The Porter-Cologne Act divided the State into nine Water Quality Control Regions for administrative purposes. Each region has its own, autonomous, Regional Water Quality Control Board which the State Board controls through funding. Each Regional Board is responsible for monitoring and enforcement of regulations for both surface and ground water at sites within its region not regulated by another agency. For example, sites regulated by the Regional Boards would include mine waste piles and geothermal wells when no drinking water supplies are threatened. In the latter case, the Department of Health Services has jurisdiction.

County Health Departments are a "catch-all" for sites that the other agencies do not regulate. The County Health Departments and the Regional Water Quality Control Boards may be viewed as being on the same administrative level. Which agency has the regulatory responsibility for a given site is determined on an individual site basis.

The above discussion describes the diffuse nature of hazardous site monitoring and regulation in California. Currently, there is some discussion in the State government about creating a Department of Toxic Substances to organize hazardous site administration within the State on a uniform basis. The Department, if created, would have the primary

responsibility for enforcing the provisions of RCRA, including the "cradle to grave" waste tracking system, and Superfund. The Department would also be responsible for monitoring and regulating landfills and other sites with the potential to degrade water quality (including ground water quality) on a statewide basis.

VIII. Oklahoma

Oklahoma is similar to Colorado in that there are several acts and agencies which have some responsibility from ground water protection. The Department of Health, however, has the responsibility for the interim enforcement of RCRA from EPA. The Department of Health is somewhat unique in that they were the only state agency contacted which routinely examines all the data they receive with the Students t-test as specified in RCRA. (Most states only do this with problem sites.)

IX. Description of Case Study Data Records

Ground water quality data were obtained from the state regulatory agencies described earlier. These data were to serve as a basis for drawing rough conclusions regarding the general behavior of ground water quality random variables and for selecting appropriate methods of statistical analysis for regulatory purposes. Most of the data records obtained are shorter, in terms of length and number of observations, than one would like for statistical analysis. However, this data base is almost certainly the best obtainable, at present, and should be able to provide a significant start toward understanding the behavior of water quality random variables. A summary of the data records obtained is presented in Table 3.1. An expanded discussion is provided in the sections which follow.

A. Nassau County New York

A data set was obtained from Nassau County New York for 12 of the public water supply wells located within the county. These 12 wells all penetrate the Magothy aquifer, which is unconfined in the area of the well field. The Magothy aquifer underlies most of Long Island as either a confined or unconfined aquifer, depending upon location, and is commonly used as a source of drinking water. It is composed largely of very fine sand, silt, and clay with some coarse to fine sand and gravel near the bottom of the aquifer. Hydraulic conductivities in the Magothy aquifer on Long Island typically range from 0.01 to 0.04 cm/sec.

Table 3.1 Summary of data obtained from case study states.

SITE	NUMBER OF WELLS	VARIABLES # NAMES	LENGTH OF RECORD	TYPE OF FACILITY
Nassau County Long Island,	12	4 NO3-N Cl, TDS, SP CON	33-62 samples per well (irregularly) from 1950 thru 1984)	water supply wells
Babylon Landfill Long Island, New York	42 (24 well clusters)	16 NO3-N, Cl, TDS, SP CON, pH, Depth, TKN, TOC, Fe, Mn, Zn, SO4, ALK, MO2-N, NH3-N	18 monthly samples (Oct. 1975 May 1977)	municipal landfill
Courtland County, New York	13 (7 well clusters)	3 NO3-N, Cl, Depth	16-30 samples per well (irregularly from 1979 thru 1984)	county water quality monitoring wells
Baker Vine Hill, Acme Landfills San Francisco Bay, California	6 (Acme)	8 NO3-N, Cl, TDS, SP CON, pH, Depth, TKN, TOC	25 quarterly samples (end 1978 thru 1984)	municipal landfill (receives some hazardous wastes)
	20 (Baker Vine-Hill)	16 NO3-N, Cl, TDS, pH, Depth, TOC, COD, As, Cd, Cr, Cu, Fe, Pb, Ni, phenols, SO4	14-16 irregular samples from 1978 thru 1984	private hazardous waste ponds

cont.

Table 3.1 Continued

SITE	NUMBER OF WELLS	VARIABLES # NAMES	LENGTH OF RECORD	TYPE OF FACILITY
Laramie River Station Wheatland, Wyoming	6	27 NO3-N, Cl, TDS, pH, Depth, SP CON, TEMP, P, ALK, HCO3, CO3, F, SO4, Ca, Mg, K, Na, As, Ba, B, Cd, Cr, Cu, Fe, Pb, Hg, Se, Zn	27 quarterly samples (1977 thru 1983)	private hazardous waste ponds and landfill
Rocky Mountain Arsenal near Denver, Colorado	26	8 Cl, F Hardness SO4, Na pH, NO3 DIMP	irregular since 1955	chemical weapons mfg.
Belvidere Municipal #2, Illinois	2	8 Cl, SP CON, TDS, FE, pH, Zn, TEMP, Depth	18-48 samples (irregular quarterly from 1974 thru 1983)	municipal landfill
Kankakee County Landfill, Illinois	7 (3 well clusters)	9 Cl, TDS, FE, NH3, COD, B, Zn, TEMP, Water	24-48 (approximately quarterly from 1974 thru 1984)	county landfill
Milan Landfill, Illinois	11	8 Cl, TDS, FE, NH3, B, COD, TEMP, depth	28-37 (approximately quarterly from 1976 thru 1984)	county landfill
Ogle County, Illinois	4	11 TDS, FE, NH3, COD, B, Pb, Zn, Cd, Hg, TEMP, depth	21-29	county landfill

Nassau County, which is a part of the New York City metropolitan area, routinely samples all of its municipal water supply wells for nitrate, chloride, total dissolved solids, and specific conductance. The samples are analyzed by methods discussed in Standard Methods: For the Examination of Water and Waste Water by the American Public Health Association.

The wells, for which data sets were obtained, have been sampled between 33 and 62 times beginning in 1950. The sampling frequency was very haphazard in the 1950's, but was standardized on a yearly basis in 1960 and 1961. The sampling frequency was further refined in the early 1970's to semi-annually. However, sampling a single well as many as 11 times in a single year was also done from about 1960. The reasons for these intensive sampling "spurts" on a particular well are unclear.

B. Babylon Landfill, Long Island, New York

The Babylon landfill has served the town of Babylon, New York, as a municipal waste disposal site since 1947. Babylon is located within Suffolk County on south central Long Island and has a population of approximately 300,000.

The United States Geological Survey (USGS) conducted an extensive investigation of the contaminant plume associated with the Babylon landfill in the early 1970's. This study revealed that the plume was located in a highly permeable ($K = 0.06$ to 0.2 cm/sec), homogeneous, unconfined, glacial outwash aquifer that underlies a large part of central Long Island. The USGS was very thorough in its study of the plume in that it was able to define a three dimensional picture of the plume by using clusters of wells to sample the aquifer at three different depths. The USGS study did not provide a large enough ground water quality data base for use in this study, but the Suffolk County Department of Health Services did use the USGS wells in a later ground water quality study which provided a large enough data set for use in the current project.

The Suffolk County Department of Health Services used the USGS wells as part of a regional planning study conducted between 1975 and 1977 under section 208 of PL92-500, "The Clean Water Act." As mentioned before, all the sampling was done in a highly permeable, homogeneous, unconfined aquifer in a known contaminant plume. The monitoring network consisted of 24 well clusters spaced from the edge of the landfill to the end of the plume 10,000 feet down gradient from the edge of the landfill. The well clusters consisted of one to three wells sampling the relatively thin (75 feet thick) aquifer at its upper, middle, and lower levels with the single wells all sampling the aquifer at its middle level.

Eighteen samples (approximately monthly) were taken from the end of October 1975 to the beginning of May 1977 and analyzed for 16 different variables. The variables included were the following: nitrate, chloride, total dissolved solids, specific conductance, pH, water table elevation, total kjeldehl nitrogen, total organic carbon, iron, manganese, zinc, sulfate, alkalinity, nitrite and ammonium. The samples were analyzed according to methods set forth in the EPA Manual of Methods for Chemical Analysis of Water and Wastes (1974).

C. Courtland County New York

Courtland County is a largely rural county in west-central New York. The area of study encompasses the 10 square mile Otter Creek-Dry Creek basin. This basin is primarily agricultural (dairy farms) in its upper reaches and contains the town of Courtland (population 20,000) at its lower end.

A data set was obtained from the Courtland County Health Department for 7 ground water monitoring well clusters. These well clusters were installed by the USGS in the mid-1970's as part of a ground water modeling effort.

Each of the 7 well clusters used by the Department of Health to monitor ground water quality consists of one shallow (20-25 ft.) well and one deep (45-50 ft.) well which sample the same aquifer. The aquifer sampled is a fairly uniform glacial outwash aquifer containing mostly sand and gravel with some silt and clay lenses. Hydraulic conductivities for the aquifer are very high and uniform, commonly being between 0.3 and 0.4 cm/sec. The wells have been sampled on an irregular basis between 16 and 30 times from late 1979 through 1984 for nitrates, chlorides, and depth to water table.

D. Baker-Vine Hill and Acme Waste Disposal Sites, San Francisco Bay Region, California

The Baker-Vine Hill and Acme sites are located approximately 20 miles north-northeast of Oakland, California. The sites are approximately 1 mile south of Suisun Bay along Pacheco and Walnut Creeks, approximately 1 mile east of Martinez, California.

The sites are underlain by a heavy clay ($K = 10^{-7}$ to 10^{-8} cm/sec) called "bay mud" with peat and sand lenses occurring irregularly over the entire site. The sites are essentially saturated with the water table varying from the ground surface to a few feet below the surface throughout the year. Ground water gradients on the sites occur because

of the ground water mounds caused by recharge from the sites. Thus, water moves radially outward from each of the sites. The elevation of the sites varies from sea level to about +40 feet. Monitoring efforts have concentrated in the peat and sand zones since the hydraulic conductivity is greater in such zones ($K = 10^{-3}$ to 10^{-6} cm/sec), contamination would be expected to appear there first.

The Acme landfill, which has been in operation since 1973, is monitored by 6 wells spaced around the site boundaries. The wells have each been sampled 25 times on a quarterly basis from late 1978 through 1984 for a total of 8 different variables. The variables sampled include nitrate, chloride, total dissolved solids, specific conductance, pH, depth to water table, total kjeldahl nitrogen, and total organic carbon.

The Baker-Vine Hill site is located about 0.5 miles southwest of the section of the Acme site which receives hazardous waste. The portion of the Acme site adjacent to the Vine Hill site receives only solid waste. The Baker-Vine Hill site is monitored by 20 wells spaced around the boundaries of the 2 adjacent sites (the Baker site and the Vine Hill site). These wells have been sampled 14-16 times on an irregular basis (2-3 samples per year) since 1978. The number of variables sampled has varied from 13 to 16, depending on the date the sample was taken. The variables sampled have included nitrate, chloride, total dissolved solids, pH, depth to water table, total organic carbon, chemical oxygen demand, arsenic, cadmium, chromium, copper, iron, lead, nickel, phenols, and sulfates. The sites have been in operation since about 1971.

Samples for both the Acme and the Baker-Vine Hill sites were analyzed in accordance with EPA documents SW-846 (Test Methods for Evaluating Solid Waste-Physical/Chemical Methods), EPA 600/4-79-020 (Methods for Chemical Analysis of Water and Wastes), and/or Standard Methods: For the Examination of Water and Waste Water by the American Public Health Association.

E. Laramie River Station

The Laramie River Station is owned by the Basin Electric Power Cooperative and is located near the town of Wheatland, Wyoming, in the southeast portion of the state. The station is a coal-fired electric generating facility that has had a ground water monitoring program since early 1977. The purpose of the monitoring system is to detect possible ground water contamination from evaporation ponds and a landfill used to dispose of fly ash and exhaust scrubber sludge generated by the plant.

The aquifer in the most danger of contamination is a shallow unconfined aquifer (approximately 10 feet below the ground surface on the plant site) which underlies the plant and much of the surrounding area as well. The aquifer is located in three distinct formations; 1) a fine grained sandstone of moderate permeability ($K = 10^{-3}$ to 10^{-4} cm/sec) known as the Arikaree formation, 2) deposits of coarse sand and gravel of higher permeability ($K = 0.02$ to 0.2 cm/sec) known as terrace deposits which overlie the Arikaree formation, and 3) flood plain deposits of coarse sand and gravel in the Laramie River flood plain ($K = 0.07$ to 0.4 cm/sec) which also overlie the Arikaree formation. The evaporation ponds and landfill directly overlie only the Arikaree formation and small parts of the terrace deposits, but the gradient of the aquifer is such that ground water flow now occurs from the plant site towards the Laramie River through all three formations. The Laramie River is approximately 1.5 miles from the evaporation ponds and landfill.

The ground water monitoring system providing data for the current study consists of two upgradient and four downgradient wells. Records of 27 quarterly samples for each of these wells (second quarter of 1977 through the fourth quarter of 1983) for 27 different variables have been obtained for analysis. Additionally, quarterly samples for another 13 wells which have been installed beginning in the fourth quarter of 1980 are available.

Samples were analyzed for the following variables: nitrate, chloride, total dissolved solids, specific conductance, pH, depth to water table, water temperature, phosphorus, alkalinity, bicarbonate, carbonate, fluoride, sulfate, calcium, magnesium, potassium, sodium, arsenic, barium, boron, cadmium, chromium, copper, iron, lead, mercury, selenium and zinc. These variables all analyzed according to methods described in Methods for Chemical Analysis for Water and Wastes (EPA 600/4-79-020).

F. Rocky Mountain Arsenal, Colorado

The Rocky Mountain Arsenal near Denver, Colorado, is a highly contaminated and extensively studied hazardous waste disposal site. The pollution problem stems largely from the disposal of hazardous materials (waste products from chemical weapons manufacture) in unlined ponds.

The RMA is located in the Denver Basin, a structural depression approximately 120 miles north to south and 70 miles east to west, filled with sediments to a depth of 15,000 ft. composed of limestone, sandstone, shale, and conglomerate.

The aquifer materials beneath the RMA are of two types. First, there are alluvial channels of fairly high hydraulic conductivity, up to about .9 cm/sec. These channels serve as conduits to move ground water through areas of less permeable material. The other important aquifer material is referred to as the Denver sands. The hydraulic conductivity of the Denver sands ranges from about 10^{-4} cm/sec to about 10^{-3} cm/sec.

Both water quality data and hydrogeological information have been provided by the U.S. Army in support of the project. The water quality variables which have been monitored to the greatest extent are chloride, fluoride, nitrate, sodium, hardness sulfate, and diisopropylmethyl-phosphonate (DIMP). DIMP is unique to RMA since it is a byproduct of the manufacture of nerve gas. Data from 26 wells have been obtained to date. The frequency of monitoring is variable; however, an adequate number of samples exist to roughly characterize the stochastic behavior of some variables.

G. Illinois

The Belvidere Municipal Landfill #2 is located in Boone County and operated by the City of Belvidere and Boone County. The landfill was originally permitted in 1974 for municipal wastes and processed sludges. The site covers 34 acres and is operated by the area fill method. The site is underlain by glacial till over glacial outwash. The monitoring program consists of two wells sampled roughly quarterly for total dissolved solids, iron, chloride, specific conductance, pH, zinc, temperature, and depth to water.

The Kankakee County Landfill is located in Otto Township and is operated by Waste Management, Inc. The landfill was originally permitted in 1975 for municipal refuse (286,000 cubic yards/year) but the permit has been supplemented to allow various additional wastes. The site covers 82 acres and the method of operation is trenching. Estimates of permeability range from 4.1×10^{-8} to 1.1×10^{-7} cm/sec, and ion exchange capacity is approximately 9.5 milliequivalents $\text{NH}_3/100$ grams of soil. The soil is comprised mostly of clay with some silt and sand. Ground water movement is east to north-east with a drop of approximately 17 feet in water table elevation across the site. Depth to water table varies between approximately 3 and 20 feet. The monitoring program consists of three pairs of wells each with a shallow screen and a deep screen. Quarterly sampling is performed for total dissolved solids, chloride, iron, and barium, ammonia, COD, zinc, temperature and depth to water.

The Milan Landfill is located near east St. Louis in St. Clair County, Illinois. The original landfill was granted a permit in 1974

and closed in 1978, with a new permit granted in 1978. The site is approximately 300-400 acres in extent and is underlain by sand and gravels or clays at depths from 2 to 25 feet. Ground water flow is from the northeast to southwest at velocities of approximately 9 to 30 feet/year. Aquifer permeability is approximately 3×10^{-3} cm/sec, and the depth to water table is 5 to 10 feet. The monitoring program consists of quarterly sampling at 11 wells for pH, specific conductance, iron, total organic carbon, chloride, ammonia, water temperature and depth.

The Ogle County Landfill is located at Davis Junction and operated by Browns Ferris Industries. The landfill was originally permitted in 1975 and developed in 1976 for general solid wastes. The site covers 162 acres. The maximum permeability is 1×10^{-7} cm/sec, and ion exchange capacity ranges between 17.7 and 20.0 milliequivalents/100 grams of soil. The soil profile is silt loam topsoil (2-4 feet), overlying silt loams, silty clay, and clay. The monitoring program consists of four wells (one upgradient, three downgradient) sampled quarterly for total dissolved solids, iron, ammonia, lead, zinc, cadmium, mercury, COD, barium, temperature, and depth to water.

X. Summary

Based on an examination of the case study states, one would conclude that ground water quality regulation is generally handled in a loosely organized fashion by several state agencies. State laws and regulations dealing with ground water quality management generally have the same goals as federal law and regulations but may be quite different in form.

The same four objectives of monitoring which were listed in Chapter Two for the federal level are also appropriate for the state level. Current monitoring activities by states focus on the second objective, determination of permit compliance, and the third objective, detection of ground water contamination.

States vary in their approach to statistical analysis of monitoring data. Routine statistical analysis of all ground water quality data is not yet common. In light of RCRA regulations, however, some states are beginning to use statistical tests, especially t-tests, to check for changes in ground water quality at permitted (regulated) facilities.

Since ground water quality monitoring for regulatory purposes is a fairly recent requirement, existing data records are fairly short; and statistical analyses, especially for characterizing the behavior of

ground water quality variables will be difficult for the near future. This problem will be discussed in more quantitative terms in later chapters.

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CHAPTER FOUR

GENERAL CHARACTERISTICS OF GROUND WATER QUALITY RANDOM VARIABLES

I. Introduction

Selection of appropriate statistical techniques for analyzing ground water quality data requires an understanding of the behavior of the random variables of concern. Without such an understanding, there exists uncertainty in whether characteristics of the data would satisfy the underlying assumptions of the statistical techniques chosen. When the assumptions of the statistical techniques are violated, the results of the analyses are questionable.

For choosing statistical techniques for trend detection analysis (the primary regulatory objective), three classes of assumptions are particularly important: 1) presence or absence of seasonality, 2) normality or nonnormality, and 3) presence or absence of serial dependence (autocorrelation). This chapter examines these three classes of assumptions for ground water quality random variables by reviewing the results of previous studies which have been reported in the literature and by analyzing the case study data described earlier.

Table 4.1 shows the number of wells from each state which were selected for data analysis. The table also contains a breakdown of wells by variable. A total of 39 wells and 15 variables were considered. The data analysis consisted of calculating basic summary statistics and testing for trend, seasonality, normality, and serial correlation. The test procedures are briefly described in subsequent sections and discussed in detail in Chapter Five. Complete results of the analyses are tabulated in the Appendix. Summarized results are presented in Table 4.2 and referred to throughout this chapter.

Another characteristic of ground water quality data which is very important, in both network design and data analysis, is the magnitude of error induced by the sample network design (e.g. well location) and measurement procedures utilized. The potential for data error is examined by reviewing previous studies on spatial variation in ground water quality (both horizontal and vertical) and the changes in ground water quality due to the time and volume of pumping and the type of sample collection equipment used.

The chapter also includes a brief review of previous findings on correlations between ground water quality variables.

Table 4.1 Number of wells, by state and by variables, used in case study data analysis.

State	# Wells	Variable	# Wells	Variable	# Wells
California	6	Chloride	37	Ammonia	6
Colorado	3	Total Dissolved Solids	20	Temperature	4
Illinois	10	pH	20	Boron	4
New York	13	Specific Conductance	18	Total Kjeldahl Nitrogen	3
Wyoming	7	Nitrate	16	Fluoride	3
		Sulfate	14	Hardness	3
		Iron	11	Sodium	3
		Total Organic Carbon	10		

Table 4.2 Summarized results of case study data analysis. Variables with fewer than 10 well records are not reported individually. Detailed results are presented in the Appendix.

Variable	NUMBER OF WELL RECORDS EXHIBITING									
	Trend		Seasonality		Normality				Serial Correlation	
	Yes	No	Yes	No	Chi-Squared	Skewness	Yes	No	Yes	No
Chloride	20	17	6	31	23	14	18	19	0	7
Total Dissolved Solids	10	10	1	19	13	7	10	10	5	11
pH	11	9	1	19	8	12	13	7	1	15
Specific Conductance	8	12	0	18	11	7	11	7	2	8
Nitrate	11	5	1	15	11	5	6	10	2	1
Sulfate	4	10	0	14	4	10	6	8	1	9
Iron	5	6	1	10	5	6	2	9	0	6
Total Organic Carbon	2	8	0	10	6	4	3	7	1	5
All Variables (listed in Table 4.2)	87	85	14	158	92	80	76	96	17	101

II. Seasonality

The technical literature was reviewed to determine whether seasonal patterns have been observed in ground water quality variables and to determine the reasons for their occurrence where possible. Presented here is a summary of reported examples and general conclusions on seasonality in ground water quality variables.

Pettyjohn (1976, 1982) presents a detailed account of seasonal patterns observed in chloride concentrations in an alluvial aquifer located in the floodplain of the Olentangy River in central Ohio that has been impacted by an oil brine disposal site. Chloride concentrations were a function of the intermittent flushing of contaminants from the disposal site into the ground during recharge events. The mass of contamination tended to enter the ground water, remain fairly intact, sink to the bottom of the aquifer, and then move towards the river. This resulted in maximum chloride concentrations occurring at different depths during different parts of the season. However, in general, highest chloride concentrations were at shallow depths during the fall and at deep depths during the spring. The magnitude of change in concentration per year depended on the length of time since the disposal site closed and the frequency, duration, and intensity of recharge events.

Schmidt (1977) discusses the factors that cause variations in ground water variables, reviewing three examples of reported seasonality. First, seasonal variations of approximately 10 mg/l per year were observed in nitrate concentrations in municipal wells located in East Yorkshire, England. Maximum nitrate concentrations occurred during late spring to early summer, while minimum concentrations occurred during fall. The suggested cause of the seasonal changes was the input of nitrates from surface soils that contained agricultural fertilizers. Second, season nitrate variations were observed in municipal water supply wells located at Delano, California. The aquifer is unconfined and comprised of alluvial deposits with water table depths ranging from 100 to 150 feet. Average nitrate concentrations ranged from 20-30 mg/l in the spring to 60-70 mg/l in the fall. The seasonal variation in nitrate concentrations was attributed to changes in ground water table levels, in that rising water table levels intercepted nitrates in the unsaturated soil above the water table. Third, nitrate and chloride concentrations showed seasonal variations in municipal water supply wells located in the northwestern part of Fresno, California. The wells are located in alluvial material with water table depth approximately 100 feet. Nitrate concentrations varied from 12 mg/l to 40 mg/l and chloride concentrations from 22 mg/l to 35 mg/l, in the winter and spring, respectively. The seasonal variation was attributed to differences in hydraulic head at the times of well pumping for sample collection.

Spalding and Exner (1980) examined seasonality in ground water quality variables from a sand and gravel aquifer in Nebraska's Platte Valley where water table depths were less than 10 feet. The data came from 53 wells sampled 10 times between July 1975 and July 1976. Results were presented for nitrate and sulfate concentrations only. However, sulfate concentrations were highly correlated to total dissolved solids, magnesium, sodium and calcium. Hence, these variables may also be assumed to exhibit seasonality. The seasonal pattern and magnitude of concentration change was related to the well location and degree of contamination. For wells located near the Platte River, both nitrate and sulfate concentrations peaked in late winter to early spring and varied from 0.1-1.2 mg/l and 200-300 mg/l, respectively. Seasonal variations were the result of water inputs into the aquifer from the river which had increased concentrations due to overland runoff and the large numbers of waterfowl that resided on the river. For wells located away from the river and in unimpacted areas, peak concentrations for both nitrate and sulfate concentrations occurred from November to April and ranged from 0.1-0.5 and 200-250 mg/l, respectively. For wells that had been impacted by agricultural activities, mainly irrigation, concentrations peaked in September and October, and varied from 5-30 mg/l for nitrates and 300-500 mg/l for sulfates. The time lag between peak concentrations and time of year of major irrigation activities for the impacted wells was attributed to transient times in the vadose zone.

Rajagopal and Talcott (1983) observed seasonal variations in nitrate concentrations for shallow (less than 30 meter depth) non-public water supply wells located in Iowa. No seasonal changes in nitrate concentrations were observed in public water supply wells (both shallow and deep) or in deep non-public water supply wells. The results showed nitrate concentrations of 10-20 mg/l in winter, rising to peak concentrations of about 56 mg/l in April to July and declining to 10-20 mg/l by August. A proposed cause of the seasonal pattern was the input of spring runoff from agricultural areas into the aquifer.

Given these observed seasonal patterns, a few general conclusions can be drawn. Ground water quality variables, especially in shallow highly permeable aquifers, may exhibit seasonal patterns. The shape and magnitude of concentration patterns will probably be directly related to characteristics of ground water recharge events, in particular the time of year, frequency, magnitude, duration, variable concentration, and source of recharge events. Often, the shape of seasonal concentration changes is roughly sinusoidal, but shapes are highly variable within any year or between different years.

The case study data were checked for seasonality as follows. First, time series plots of the data were visually inspected for

trend. If a possible trend was apparent, a linear regression of concentration versus time was performed, and the parameter estimates were examined for significance. If the significance level of the slope was less than 0.3, the trend was removed from the data.

Following the detrending step, the residuals were examined for seasonality using 1) visual inspection of time series plots and/or box and whisker plots of concentration versus quarter and 2) Kruskal-Wallis test (nonparametric equivalent of analysis of variance) at the 95% confidence level. As indicated in Table 4.2, of the 193 cases examined, only 15 exhibited significant seasonal behavior. The variable which was most often seasonal was chloride, showing seasonal behavior in 6 out of 37 cases.

III. Normality

The literature was reviewed to determine whether observed ground water quality variables have exhibited normal frequency distributions. The conclusions stated below are based principally on the following studies which presented general statistical characteristics for ground water quality variables in individual states: Missouri, Feder (1979); Michigan, Cummings (1980); Northern Idaho, Parilman et al. (1980); Wisconsin, Kammerer (1983); Iowa, Rajagopal and Talcott (1983); Kansas, Spruill (1983); Nebraska, Engberg (1984); and Sacramento Valley, Hull (1984). Two problems associated with these studies that made the development of conclusions difficult were: 1) differences format in which summary statistics were presented, and 2) failure to apply quantitative statistical techniques to test whether frequency distributions were normal.

It appears that many ground water quality variables are not normally, or even symmetrically, distributed. The frequency distributions observed tended to be skewed right, with the degree of skewness varying considerably. Some ground water quality variables had distributions which were fairly symmetric about a central value (e.g. mean or median) between the minimum value and an upper percentile (e.g. 90th), but also had a few "very" large values which resulted in a skewed-right distribution. Two possible reasons for these large values are: 1) measurement errors, in which case the values should be disregarded, or 2) ground water contamination, in which case the high values may belong to a "population" different from that of the remaining sample values. In either case, variables that have symmetric frequency distributions, except for a few large values, might be assumed to be approximately normal if the large values were excluded. In practice, of course, one must carefully justify and document the removal of any recorded values.

Some ground water quality variables have data that contain numerous values equal to zero or the detection limit. This often results in frequency distributions that are extremely skewed to the right. For example, many organic or toxic substances may have estimates of the mode and median equal to zero or the detection limit.

Some of the factors which influence the type of frequency distribution and values of the distributional parameters for ground water quality variables are: geology, aquifer properties, land use, amount of contamination, depth of water table, measurement procedures, and well type.

Case study data were examined for normality using 1) visual inspection of frequency histograms and/or normal probability plots, 2) chi-squared goodness-of-fit tests, and 3) skewness tests. Both of the latter tests were performed at the 5% significance level (95% confidence level). Table 4.2 indicates that the chi-squared test found 92 of 172 cases to be normally distributed while the skewness test found only 76 cases to be normally distributed. It will be shown in Chapter Five that the skewness test is preferred for this application, providing more power to detect nonnormality than the chi-squared test. The variable which was most often found to be normally distributed was specific conductance with normality found in 11 out of 18 cases, according to the skewness test. The "least normal" variable was nitrate, showing normality in 6 out of 16 cases. (As an aside, normal behavior for pH would actually imply lognormal behavior of the concentration random variable.)

IV. Serial Dependence

The objective of the literature review on serial dependence was to determine whether samples of ground water quality data have been found to exhibit serial correlation. All sampling frequencies reported were quarterly or less frequent. Only two studies were found in which autocorrelation coefficients had been estimated. One study dealt with ground water quality variables, and the other dealt with ground water levels.

Hull (1984) estimated autocorrelations for nitrate and dissolved solids concentrations obtained from shallow (depth to water table varying from 10 to 80 feet) ground water wells in the Sacramento Valley, California. Nitrate concentrations from 62 wells were studied; dissolved solids concentrations from 140 wells were studied. Dissolved solid concentrations were estimated as a function of measured specific conductance. The data for each well were standardized to a mean of zero and standard deviation of one. A mean annual concentration was

then estimated for each hydrochemical species. Estimated annual lag-one autocorrelation coefficients varied from 0.3 to 0.5 for nitrates and were consistently near 0.3 for dissolved solids.

Law (1974) conducted a stochastic analysis of monthly ground water levels in 84 wells from 22 states west of the Mississippi River. Lag-one, lag-two, and lag-three monthly autocorrelation coefficients were estimated after removal of periodicities in both the mean and standard deviation of the original series. The distribution for all wells of the lag-one autocorrelation coefficients had a mean of 0.79 and was skewed left, while lag-two and lag-three autocorrelation coefficients had means of 0.65 and 0.56, respectively. Both the lag-two and lag-three coefficients had symmetric distributions. No spatial patterns between wells were found (i.e. there were no differences in autocorrelations based on aquifer types).

Because of the limited number of reported studies examining autocorrelations in ground water quality data, it is very difficult to determine whether quarterly sampled ground water quality data exhibit serial dependence. However, quarterly ground water levels have been observed to be autocorrelated (e.g. mean equal 0.56) and ground water quality is often correlated with water table levels (Schmidt, 1977; Spalding, Exner, 1980). Therefore, there exists a potential for quarterly ground water quality data to exhibit serial dependence.

The case study data were tested for serial correlation by computing the lag-one autocorrelation coefficient for those records where data were evenly spaced in time, i.e. quarterly data with few missing observations. The calculated coefficients $r(1)$ were compared with 95% confidence limits $r(1) \pm \frac{1.96}{\sqrt{n}}$. Values of $r(1)$ falling outside these limits were said to be statistically significant.

Of the 118 cases examined, only 17 showed significant serial correlation. Furthermore, since most of the records examined were very short, it was not possible to deseasonalize data prior to testing for serial correlation. Therefore, much of the apparent autocorrelation could be due to seasonality. However, eight cases were found in which serial correlation was significant but seasonality was not.

V. Sampling Error

Sampling errors in water quality monitoring systems may be defined as errors associated with network design, which includes determination of station location, sampling frequency, and variable selection. Station location is particularly important in ground water monitoring

systems and may be divided into macrolocation and microlocation. Macrolocation is the site location in reference to the entire area of interest, and for ground water monitoring is the number and location of monitoring wells. The determination of well location should depend primarily upon horizontal spatial patterns in ground water quality variables. Microlocation refers to the specific local point of sample collection at a particular macrolocation, and for ground water monitoring is the length and depth of the well screen. The determination of ground water microlocation is dependent primarily upon vertical spatial patterns in ground water quality variables. Two factors that affect both macrolocation and microlocation are the volume of water per sample removed from the aquifer and the portion of the aquifer which is sampled. These factors are dependent upon the pumping scheme used (time and volume) and the aquifer properties, such as hydraulic conductivity, non-homogeneity and anisotropy. The remaining portion of the sampling error section presents information on vertical and horizontal spatial patterns in ground water quality variables and patterns in changes of ground water quality concentrations due to the amount of time or volume of well pumping. The information consists of patterns reported in previous studies which may affect the magnitude of ground water quality data error.

A. Vertical Patterns

Vertical patterns in ground water quality concentrations that have been reported were reviewed to determine their shape, amount and causes. The majority of previous work on vertical concentration patterns deals with shallow unconfined permeable aquifers. However, this should not preclude the possibility of vertical patterns in other types of aquifers.

Childs et al. (1974) examined waste migration patterns from septic tank and tile field systems surrounding Houghton Lake, Michigan. The site consisted of sandy soils with water table depths of 0 to 5 feet and wells penetrating to depths of 24 feet below the water table. Vertical concentration changes were observed in nitrate, chloride and phosphorus (over a 20 foot distance below the water table). The magnitudes of these changes were 2-14 mg/l, 20-80 mg/l and 0.01-0.5 mg/l, respectively. The vertical concentration changes were a function of the loading rate and recharge events at the waste source, local hydrology, chemical-absorption, soil microbiology, and regolith texture and fabric.

Eccles and Bradford (1976) and Eccles (1979) reported that nitrate and dissolved solid concentrations decreased with depth below the water table for ground water in the Santa Ana Basin, California. The aquifer was mainly sand and gravel, had depths to water table of 20 to 300

feet, and was sampled in the autumn of 1974 and late spring 1975. The suggested reasons for vertical patterns were land use, point source contamination, and recharge from rivers. It was also stated that the use of high capacity wells may lead to confusion in data interpretation because of the large volume of water sampled, use of wide screens, variation in hydraulic conductivity with depth, and varied well screen efficiency.

Ragone et al. (1980) examined ground water in sewered and unsewered areas of Nassau County, New York, consisting of sand, gravel, silt, and clay. Median nitrate concentrations from 0-3 meters below the water table were significantly lower in sewered areas than in unsewered areas. In general, nitrate concentrations decreased with aquifer depth in both sewered and unsewered areas.

Spalding and Exner (1980) analyzed ground water data from 53 wells, sampled 10 times between July 1975 and July 1976, in a 62 square kilometer area in the Platte River Valley, Nebraska. Concentrations for nitrate, silica, sulfate, total dissolved solids, sodium, magnesium, and potassium decreased with depth in ground waters that were downgradient of cultivated and irrigated fields, with decreases most pronounced in areas undergoing ground water pumping for irrigation use. For example, nitrate concentrations changed from 300 to 3 mg/l and total dissolved solids from 700 to 300 mg/l from a depth of 2 to 22 meters, respectively. Magnesium and potassium showed vertical changes regardless of the upgradient land use and site specific variability in vadose zone layer composition.

Junk et al. (1980) reported results for organic constituents for the same area investigated by Spalding and Exner (1980). Dissolved organic carbon concentrations decreased from 3.0 to 1.5 mg/l from a depth of 5 to 60 feet, respectively. The suggested reason was migration through the vadose zone and aquifer dispersion.

Rajagopal and Talcott (1983) analyzed ground water quality data from numerous wells in Iowa. Increased mean concentrations with depth were observed for chloride, sulfate, hardness, non-carbonate hardness, dissolved solids, specific conductance, and water yield. Decreased mean concentrations with depth were observed for nitrate. The proposed reason for the vertical patterns for variables with increasing concentrations with depth was the highly mineralized nature of Iowa ground water. Higher nitrate concentrations at shallow depths were thought to result from nonpoint source agricultural contamination.

Nazar et al. (1984) examined vertical concentration patterns for inorganic and organic variables in upgradient and downgradient wells at an eight-acre uncontrolled hazardous waste site. The aquifer consisted

of alluvial material with water table depths between 10-20 feet. The site location was not specified. For inorganic variables (ammonia, iron, chloride, and sulfate), concentrations first increased with depth below the water table, peaked at 10 feet below the water table in upgradient wells and 20-30 feet below water table in downgradient wells. Concentrations then decreased with depth to concentrations below those found at the water table. For organic variables (fenac, toluene, 1,2 dichloroethane, and chlorobenzene), concentrations decreased with depth at upgradient wells while at downgradient wells, concentrations first increased with depth, then peaked at 10-20 feet below the water table, and then decreased with depth.

Pettyjohn (1976, 1982) observed that the vertical patterns in chloride concentrations varied seasonally for wells that had been impacted by an oil brine disposal site in Ohio. The results showed chloride concentrations increased with depth in the spring, and decreased with depth in the winter. These seasonal vertical concentration changes were the result of the magnitude and time of occurrence of recharge events.

B. Horizontal Patterns

Horizontal spatial patterns in ground water quality concentrations examined on a local spatial frame tend to vary considerably for different variables at the same site and for the same variable at different sites. Stollar et al. (1983) found that ground water quality variables from a food-grade waste disposal site in Lawrence, Kansas, exhibited an exponential decay in concentration with distance away from the center of a plume. Birden and Cech (1981) estimated spatial correlations, at an approximate distance of 30 meters, to be between 0.1 and 0.5 for bacterial concentrations which were the result of septic field inputs. Horizontal spatial patterns in ground water quality concentrations tend to be a function of the type and magnitude of the contamination source and specific site characteristics (e.g. hydrogeology).

On a regional level, horizontal gradients in ground water quality may exist as a result of differences in geology, hydrogeology, and land use, examples of which follow. Two problems with developing statements about horizontal patterns in ground water concentrations are: 1) the limited number of well locations used in most studies and 2) the limited use of computerized data analysis techniques to quantify horizontal concentration gradients.

Hull (1984) presented ground water quality data from a 4,400 square mile area of Sacramento Valley. The aquifer consisted of sand

and gravel materials with depths to water table ranging from 0-40 feet. Concentrations ranged horizontally from: 85-592 mg/l for dissolved solid; 5.4-150 mg/l for chloride; 7.0-82 mg/l for sulfate; 11-22 mg/l for silica; 11-53 mg/l for calcium; 4.7-40 mg/l for magnesium; 6.3-101 mg/l for sodium; and 6.5-101 mg/l for bicarbonate. Schwartz and Muchlenbachs (1979) reported ranges in ground water concentrations over a 6,300 square kilometer area of south eastern Alberta of 10-1200 mg/l for chloride; 10-750 mg/l for sulfate; 400-1200 mg/l for sodium; and 600-1400 mg/l for bicarbonate. Feder (1979) used a four-level analysis of variance to analyze ground water quality data obtained from a reconnaissance survey conducted in Missouri to determine the major sources of variation in each variable. The results showed that major variations in ground water quality for most variables occur over large geographic regions (level 1 and 2). Only magnesium, lithium and barium exhibited significant variation within four square kilometers (level 3), and only chloride and aluminum exhibited significant variations associated with sample and analysis methods (level 4). Eccles (1979), in a study of alluvial ground water in the Santa Ana Basin, California, found that nitrate concentrations varied from 1 to 5 mg/l per mile and dissolved solid concentrations varied from 30 to 200 mg/l per mile. Edelman and Buckles (1984) examined ground water quality from the San Luis Valley in southern Colorado and found horizontal spatial variability in nitrate-nitrite concentrations of 3.5-10 mg/l per 5 to 10 miles and in specific conductance of 250-2250 umhos/l over 3 to 15 miles distances.

There may exist significant differences in ground water quality concentrations based upon the geologic formation of an aquifer. This type of spatial concentration pattern is described in the following studies: 1) ground water quality concentrations were larger in bedrock aquifers than in glacial aquifers in Michigan (Cummings, 1980); 2) differences exist in ground water quality concentrations between the three major aquifer types found in Nebraska (Engberg, 1984); 3) differences in ground water quality occur over a portion of the Ogallala aquifer (Kroethe, 1982); and 4) ground water quality differs between the mineral belt zone compared to the non-mineral belt zone in central Colorado (Klusman, Edwards; 1972).

Another factor that may significantly effect the quality of ground water on a horizontal spatial frame is the type of land use. The major types of land use which reportedly affect ground water quality are agricultural activities (irrigation and fertilizers) and point sources.

Nightingale and Bianchi (1974) compared ground water quality in two arid irrigated areas near Fresno-Clovis, California. One area imports high quality surface water for irrigation purposes, while the other area upgradient of the first uses local pumped ground water for

irrigation. The aquifer material is mainly alluvial with well depths between 30 and 60 meters. Samples were collected from 154 pumping wells in August and September 1972. Concentrations were significantly different between the two areas for nitrate, chloride, and specific conductance with concentrations in the area that used local pumped ground water being 18.6, 91.8, and 9.5 percent higher, respectively, than those areas using imported high quality water.

Exner and Spalding (1979) compared differences in ground water quality under pristine conditions to that affected by nonpoint contamination and point contamination in Holt County Nebraska. Samples were collected by pumping at 272 wells in the summer of 1976. Mean concentrations for the pristine, nonpoint, and point contamination areas, respectively, were: nitrate (2,36,43 mg/l), chloride (0.6,4.6,6.9 mg/l), total dissolved solids (134,180,222 mg/l), and sulfate (2.2,8.4,13 mg/l), respectively.

Spalding and Exner (1980), for the site described earlier, found that concentrations for nitrate and total dissolved solids were larger in pristine areas compared to irrigated areas, differing by 0.1-33 mg/l and 557-2210 mg/l, respectively.

Schmidt (1977) refers to a study in East Yorkshire, England, where in a shallow alluvial aquifer nitrate concentrations increased from 2 mg/l in an agricultural area without fertilizer application to 65 mg/l in an agriculture area with fertilizer application.

C. Effects of Pumping

Ground water quality concentrations may vary based on the amount of time or water volume pumped in a well. In addition, the time and volume pumped along with aquifer properties will determine where the sample originated in the aquifer.

Keely (1982) provides a set of generalized figures of concentration versus time and volume of pumping (Figure 1). Figure 1a suggests that the well is in a plume of limited area (volume) or the well is near the edge of a large plume; however, if concentration decreases rapidly, well contamination is suggested. Figure 1b suggests the pumping briefly encounters some small recharge source or the well is located in a fractured aquifer. A very narrow change represents a localized anomaly. Figure 1c suggests that the contamination source is external to the well, while a very rapid increase in concentration suggests well contamination. Figure 1d suggests an isolated plume while rapid concentration changes suggest well contamination.

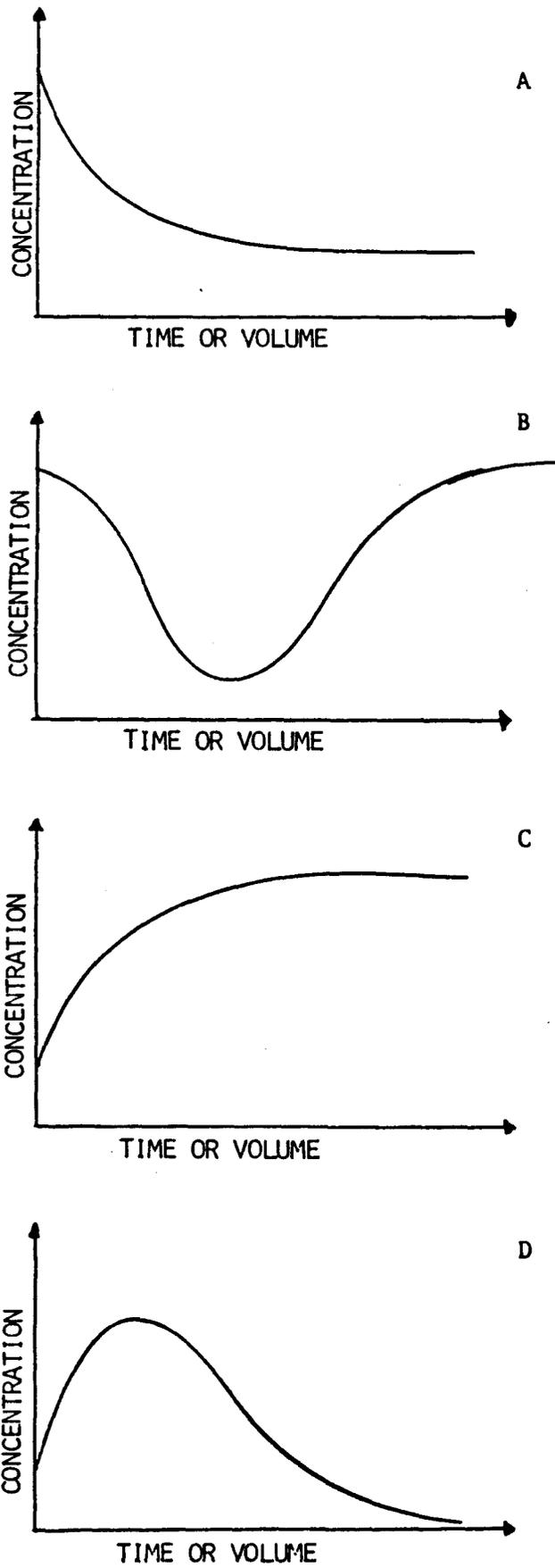


Figure 4.1 Generalized patterns in ground water quality with time or volume of pumping (from Keely, 1982).

Humenick et al. (1980) examined changes in ground water quality with time since start of pumping for an area near an in-situ uranium leach mine. Nitrate and sulfate concentration responses were similar to Figure 1b with ranges of 1-13 mg/l and 60-125 mg/l reported, respectively. Bicarbonate and temperature responses were similar to Figure 1d with ranges of 350-475 mg/l and 25-27°C reported, respectively. The time to stabilization for all variables was between 30 and 40 minutes. Factors that affected concentration changes were 1) geometric and hydraulic relationships between the pump and well and 2) bacterial processes in the well casing.

Wilson and Rouse (1983) examined variations in ground water quality during the initial pumping of wells in flood plain deposits downstream of a cyanide mill tailings area. Specific conductance and pH responses were similar to Figure 1a with ranges of 1100-2500 umhos and 6.5-6.8, respectively. Iron and manganese responses were similar to Figure 1c with ranges from 1.25-3.3 mg/l and 0.6-1.0 mg/l, respectively. The volume pumped prior to stabilization was between 2 to 5 bore volumes. The suggested reasons for concentration changes were mixing of waters from different aquifer areas and removal of stagnant water within the well itself.

Keely and Wolf (1983) conducted chemical time-series sampling for volatile organics at wells in the Lakewood Water District in the state of Washington. Concentrations of tetrachloroethylene, 1,2 trans-dichloroethylene, and trichloroethylene all showed patterns similar to Figure 1c with ranges of 10-60 ug/l, 10-30 ug/l, and 1-10 ug/l, respectively. The time for stabilization was approximately 200 minutes. The suggested cause was an external contamination source.

The relation between the time and volume pumped to the portion of the aquifer sampled has been examined. Keely (1982) presented procedures for determining the volume of water withdrawn for both radial drawdown (cylinder) and rectangular drawdown and suggests weighting concentration values obtained in time series sampling by volume. Keely and Tsang (1983) presented three techniques to model the source of water obtained from pumping wells. Papadopulos and Cooper (1967) presented a method to estimate the duration of pumping during which stagnant waters in a well are included. The applications of these techniques are highly site specific, being dependent on geologic and aquifer properties.

VI. Nonsampling Errors

Nonsampling errors in ground water quality data may result from four major sources: 1) measurement, which includes well construction

and development, sample collection, sample preservation and storage, and laboratory analysis; 2) processing, which includes data coding, computer input, storage, retrieval, screening, verification, and manipulation; 3) estimation, which includes the type of statistical estimator(s) and computer software; and 4) model, which includes probability distribution functions, models of temporal and spatial processes, and model parameter estimates. The emphasis of the review is on potential sources of measurement error in ground water quality data, in particular on sample collection.

The objective of sample collection is to provide a representative and uncontaminated water sample which can be used to estimate chemical concentrations. Three important factors in ground water sample collection that may cause data errors are: 1) the physical device or method used to obtain the water sample; 2) the time or volume of pumping needed until water quality concentrations will stabilize; and 3) the region of aquifer from which sample came. The last two factors have been discussed in the section on pumping; hence, the following reviews refer mainly to errors associated with physical devices and methods.

Gibb et al. (1981) and Schuller et al. (1981) examined ground water quality collected by different sample collection methods from wells at six different sites located in Illinois, with well depths between 16 and 30 feet and depths to water table between 0 and 16 feet. Results showed peristaltic pumps and bailing methods produced little changes in ground water quality concentrations, while air and nitrogen lift pumps caused increased pH values of up to 1.0 units and decreased concentrations of iron and zinc. Values of pH increased by 0.3 to 0.4, units while iron and zinc concentrations decreased to less than detectable levels, when filtration and preservation procedures did not occur within 7 hours of sample collection. Concentrations of iron, manganese, and zinc were sensitive to the pore size of the membrane used for filtration, while calcium, potassium, magnesium, and sodium had similar concentrations regardless of membrane pore size.

Barcelona et al. (1984) attempted to identify reliable sampling mechanisms for purgeable organic compounds and gas sensitive chemical parameters in ground water by reviewing 14 devices for sample collection comprising 5 different mechanistic categories. The results showed peristaltic (suction) mechanisms significantly changed concentrations for pH (+0.05) and specific conductance (-20 mv). Significant bias in oxygen concentrations existed between control samples and samples collected from conventional bailer (-8.5% bias), syringe sampler (-7.0% bias), gas displacement (+9.0% bias), suction (-8.0% bias) and positive displacement (-13% bias). Gas displacement and suction devices showed

statistically significant losses of purgeable organic compounds (trihalomethane) while positive displacement bladder pumps and bailers showed no significant differences.

Fetter (1983) presented results on the effect of different materials used during well drilling and construction. Wells that were drilled with a commercial organic polymer had elevated chemical oxygen demand values (370 to 740 mg/l) which decreased to concentrations between 24 to 76 mg/l after 50 to 60 days. Similar results were shown for wells drilled using bentonite, with chemical oxygen demands changing from 35-80 mg/l initially to less than 10 mg/l after 40 days.

VII. Intervariable Correlations

Knowledge of the intervariable correlation structure of ground water quality is useful for 1) the variable selection step in the design of ground water monitoring networks, and 2) the identification and explanation of aquifer zones of homogeneous behavior in terms of ground water quality. More specifically, the level of correlation among variables may be used to determine surrogate variables to sample in place of the primary objective variable(s). This is especially useful when the primary objective variable is costly to measure or has a potential for large data errors, providing for more frequent sampling of variables which are inexpensive and easy to measure. Intervariable correlations also provide the basis for regression-type sampling design procedures. The use of correlations among variables may be very useful on a site specific basis; however, care must be taken when transferring the results obtained from one geographic area or aquifer type to another.

Exner and Spalding (1979) examined correlations among ground water data from sections of Holt County, Nebraska, which have been impacted from either point or nonpoint sources. For areas impacted by point sources, significant correlations existed among dissolved solids, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, and nitrate concentrations. For areas impacted by nonpoint sources, significant correlations existed among dissolved solids, calcium, magnesium, sodium, potassium, and bicarbonate concentrations.

Spalding and Exner (1980) examined the correlations among ground water quality variables sampled in a bottomland aquifer near the Platte River in Nebraska. The results showed significant correlations ($r > 0.80$) between: 1) total dissolved solids and calcium, magnesium, chloride, and sulfate; 2) calcium and magnesium, chloride, sulfate, and nitrate; 3) magnesium and sodium, chloride, sulfate, and nitrate; and 4) sodium and sulfate. The suggested two variables which may be used to represent the other variables are sulfate and nitrate.

Marzouk et al. (1979) examined bacteria and virus concentrations in 99 samples collected from ground water in Israel and found: total bacteria correlated to fecal streptococcus ($r=0.57$); fecal streptococcus correlated to fecal coliform ($r=0.53$); and no correlation between viruses and bacteria.

Spruill (1983) examined ground water quality over the entire state of Kansas and found significant correlations between concentrations of dissolved solids, sulfate, and chloride, and also between iron and manganese.

Rajagopal and Talcott (1983) examined ground water quality data from the entire state of Iowa and found a significant correlation existed between dissolved solids and sulfate concentrations ($r=0.95$).

Cummings (1980) examined the relationship between dissolved solids and specific conductance data from natural (unimpacted) ground water in Michigan. The data could be fit by a linear model with a slope of 0.79.

Three studies that have used multivariate analysis techniques to utilize the correlation structure among ground water quality variables to define homogeneous aquifer zones are presented below. The application of multivariate techniques may be useful in assisting in the determination of macrolocation stations by defining areas of homogeneous water quality in the horizontal spatial frame.

Feder (1979) applied Q-mode factor analysis to data collected by a reconnaissance survey of ground waters in Missouri. The results suggested that ground waters of the state can be divided into four groups based on water quality: 1) a calcium-magnesium-bicarbonate water with relatively high copper levels; 2) a sodium-bicarbonate-chloride water with high potassium, lithium, aluminum, boron, rubidium, strontium, fluoride, and bromide levels; 3) a calcium-bicarbonate-sulfate water with high iron and manganese levels; and 4) a water low in total dissolved solids and trace elements.

Hull (1984) applied principal component analysis to 15 variables sampled from numerous wells in shallow ground water from the Sacramento Valley, California. Two components were identified: 1) a component representing the effects of the recharge water chemistry (accounted for 36% of total variation), which includes dissolved solids, calcium, magnesium, sodium, bicarbonate, chloride, sulfate, and negative silica; and 2) a component representing the effect of fine grained sediments on water quality (accounted for 17% of total variation) and included potassium, negative nitrate, manganese, and arsenic.

Page (1981) applied factor analysis to 23 toxic substances sampled from New Jersey ground water. The results suggested four factors which may be used to determine ground water groups: 1) pesticides (48% of variation), 2) light chlorinated hydrocarbons (30% of variation), 3) heavy metals (14% of variation), and 4) BHC beta substances (8% of variation).

Based on this review of literature, one may conclude that intervariable correlations are often quite significant and may in some cases be used to extract additional information in ground water quality studies. However, the authors caution that their use in regulatory monitoring should be undertaken with caution. Regulatory monitoring is designed to detect pollution events which would certainly change intervariable correlations. Ultimately, the manager of water quality must monitor variables which would be noticeably impacted by a pollution event.

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CHAPTER FOUR

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CHAPTER FIVE

STATISTICAL METHODS FOR CHARACTERIZING GROUND WATER QUALITY VARIABLES

I. Introduction

The recurring theme of this report is the need for detecting changes in ground water quality at regulated facilities. Water quality managers are faced with the task of selecting appropriate statistical methods for this purpose. As stated in Chapter Four, one needs to know whether the random variables of concern are normally distributed, seasonal, and/or serially correlated in order to choose appropriate methods.

One often has little or no historical data upon which to base these assumptions. One must, therefore, rely on general information such as that presented in Chapter Four and on whatever information is available regarding local hydrogeology in order to make preliminary judgements. Once data collection begins, however, more quantitative assessments of the random variables of concern can be made.

This chapter deals with methods for characterizing ground water quality random variables in terms of 1) seasonality, 2) normality and 3) serial correlation. Particular emphasis is placed on the problem of small sample sizes which is ever-present in ground water quality management.

II. Testing for Seasonality

As indicated in Chapter Four, few of the case study data records showed predictable periodic behavior (seasonality). However, other researchers have found that seasonal behavior in ground water quality is often associated with annual cycles in precipitation or recharge events, particularly for shallow unconfined aquifers and for situations where stream-aquifer interaction is strong.

For quarterly data, a reasonable form of annual cycle is for one quarter to be different from the other three. This type of cycle could easily occur in areas with high spring recharge followed by three seasons of moderate recharge. The same reasoning applies to areas with three moderate recharge seasons and one low season.

A. Student's t-test

Testing for seasonality where one season differs significantly from the other reduces to a two-sample comparison of means. A statistical test comparing two means will reject the null hypothesis, that the means are equal, in favor of the alternative hypothesis, that the means are different, if the test statistic for the observed samples has a probability level less than some pre-selected value, α . When the question being tested is that one season has a mean lower than the rest of the year, the alternative hypothesis is one-sided, and the probability represented by α occurs at the upper tail of the statistic's distribution. For an alternative hypothesis that the means are simply different, with no reason to specify which is lower, the test is two-sided. In this case, the critical areas of the test is at each end of the distribution, and α is divided equally between upper and lower tails.

The most common test to compare two means is the Student's t-test (Larsen and Marx, 1981). The statistic is

$$T_{n+m-2} = (\bar{X}_1 - \bar{X}_2) / Sp \sqrt{\frac{1}{n} + \frac{1}{m}} \quad (5.1)$$

where \bar{X}_1 and \bar{X}_2 are the sample means, Sp is the square root of the pooled variance, n and m are the number of observations in the first and second samples, respectively. The calculated T_{n+m-2} should be compared to tabulated values of the t-distribution with $n+m-2$ degrees of freedom. Tables are included in almost any statistics text.

The test assumes the data came from normally distributed populations with equal variances, but is robust against departures from normality when the sample sizes are nearly equal (Boneau, 1960). Since the number of samples in the three-season group will be close to three times the number in the one-season group, the test should not be applied in cases with strongly skewed data.

When the data are obviously non-normal, the Mann-Whitney distribution-free test may be used. It compares ranks of the two samples with the null hypothesis that the distributions of the samples are identical (Miller and Freund, 1977). For sample sizes larger than eight, the statistic is approximately normal, and its standardized value can be compared with standard normal tables. Tabulated values are available (in, for example, Owen, 1962) for the exact test for small samples.

The limiting efficiency of the Mann-Whitney test is 95.5% relative to the t-test when the assumptions of the t-test are met. Relative efficiency can be viewed as the number of samples required by the test in order to achieve the same reliability as a test assumed to be 100

per cent efficient. In the present case, the Mann-Whitney test with 100 observations is as reliable as the t-test with 95.5 observations.

The power of a test is defined as its ability to detect a difference in means when there actually is a difference.

The t statistic has a non-central t-distribution when the alternative hypothesis is true. It is indexed by Δ , the actual difference in means and by $n+m-2$, the degrees of freedom. This distribution is used to calculate power.

Table 5.1 shows the power of the t-test for differences of 1.0σ , 1.5σ and 2σ between the means where σ is the common standard deviation of the samples. To relate sample size to length of record, quarterly sampling is assumed. The numbers in the body of the table are the proportions of times the calculated t value will be outside the range of the t distribution under the assumptions of the null hypothesis. The significance level of the test is 0.025 for a one-tailed test. It is assumed that the direction of the difference is known in advance. For example, spring recharge might be expected to dilute the constituent of interest, so comparing the spring season to the remainder of the year would imply a decrease in the mean of the spring samples.

The table shows that if one season has a mean different by one standard deviation from the mean of the other three seasons, the probability of detecting the difference in 2 years is less than 0.3. After 5 years of quarterly sampling, the probability of detecting the difference is only 0.46. For example, if the mean of chloride concentration for season 1 were 10.7 mg/l and 14.8 mg/l for season 2-4 with a common standard deviation of 4.1, it is likely that the t-test would indicate no seasonality. If the mean of seasons 2-4 were 18.9 mg/l, the probability of detecting seasonality after 2 years would be 0.53, increasing to 0.957 after 5 years.

B. Analysis of Variance

When one does not have prior information to indicate which season or quarter would be different from the others and the data are not highly skewed, the familiar analysis of variance test may be used. The model assumed for this test is

$$X_{ij} = \mu + \tau_j + \epsilon_{ij} \quad , \quad i=1,2,\dots,n_j; j=1,2,\dots,k \quad (5.2)$$

where X_{ij} is the i th observation of season j , μ is the overall mean,

Table 5.1 Approximate power of Student's t-test for a one-sided interval at the $\alpha=0.025$ significance level; two-sample test with $m=3n$, assuming quarterly sampling. (Larsen and Marx, 1981)

Years of Record	Number of Observations	$\frac{\Delta}{\sigma}$		
		1.0	1.5	2.0
2	8	<0.3	0.33	0.53
3	12	<0.3	0.54	0.77
4	16	0.38	0.68	0.90
5	20	0.46	0.77	0.957
6	24	0.53	0.86	0.982
7	28	0.60	0.91	>0.99
8	32	0.66	0.946	>0.99
9	36	0.71	0.965	>0.99
10	40	0.78	0.978	>0.99
20	58	0.972	>0.99	>0.99

r_j is the effect of season j , and ϵ is the error in the observation. The null hypothesis is that the r_j 's are equal for all j . The alternative hypothesis is that the r 's are not equal (Larsen and Marx, 1981).

The test is an extension of the t-test to include k samples. Similar assumptions and constraints apply. When the alternative hypothesis is true, that is when all the season means are not the same, the statistic has a non-central F distribution. The integral is not very tractable (Larsen and Marx, 1981) but it has been approximated and tabulated by Mann (1949).

When two samples are being compared ($k=2$), the analysis of variance is equivalent to the t-test; both accept or reject the same hypotheses.

C. Kruskal-Wallis Test

In cases where the data are skewed, the Kruskal-Wallis distribution-free analysis of variance is appropriate (Hollander and Wolfe, 1973). The model is the same as for ordinary analysis of variance, $X_{ij} = \mu + r_j + \epsilon_{ij}$. The null hypothesis, all the r_j 's are equal, and the alternative hypothesis, the r_j 's are not all equal, are also the same.

The statistic, H , involves the ranks of all the observations averaged for each season. Under the null hypothesis, H is distributed asymptotically χ^2 with $k-1$ degrees of freedom.

Exact values of the statistic are tabulated for $k=4$ with at most 4 observations in each season (Iman et al., 1975). The lack of tables for larger values of n is a disadvantage, but algorithms are presented with the tables listed above that allow recursive calculation of the values. Because the probability is based on permutations of the ranks in the seasons, the calculations require large amounts of computer time or storage.

The asymptotic relative efficiency of the Kruskal-Wallis test to the analysis of variance F test is 0.955 when the underlying populations being tested are normal and the test is that the locations ($\mu+r_j$) are identical. The relative efficiency is the same as that of the two-sample Wilcoxon rank-sum test to the Student's t-test (Bradley, 1968).

III. Testing for Normality

Four tests for normality are in common usage, the chi-squared goodness of fit test (CS), the Kolmogorov-Smirnov test (KS), the skewness coefficient (b_1) and the Shapiro-Wilk test (W). The tests are described in Table 5.2.

The CS and KS tests require specification of the parameters μ and σ of the null distribution. The b_1 and W tests are origin and scale invariant and, therefore, test the null hypothesis of normality against the composite alternative hypothesis of non-normality (Shapiro et al., 1968).

The difficulty in making definitive statements about the distribution of a population from a small sample is illustrated below with portions of results from Shapiro et al. (1968). These authors compared several tests for normality, including the four listed above, in terms of their power against a variety of alternatives for samples sizes of $n=10, 15, 20, 35$ and 50 .

The results of their calculations of power for a significance level of 0.1 against an underlying population with a chi-square distribution with 4 and 10 degrees of freedom are shown in Figures 5.1 and 5.2, respectively. Figure 5.3 shows the chi-squared probability density functions. The symmetry of the distribution increases with the number of degrees of freedom, so it would be expected that the power to detect non-normality would decrease with increasing degrees of freedom. Figures 5.1 and 5.2 confirm this. The best test has a power above $.95$ against 4 degrees of freedom for $n=50$, but drops below $.75$ for 10 degrees of freedom.

The Shapiro-Wilk W statistic and the skewness coefficient are superior to the CS and KS tests for all the conditions shown. There is little difference in the power of the W statistic and the skewness coefficient. Since the calculation of W requires coefficients that are not widely tabulated (Shapiro and Wilk, 1965), the skewness coefficient is recommended.

The value of the skewness coefficient at the $.05$ and $.01$ levels are tabulated in, for example, Snedecor and Cochran (1967) and Biometrika Tables for Statisticians, Vol. 1 (1954), for sample sizes as low as 25 . Table 5.3 extends the existing table to sample sizes of 9 to 30 . Table 5.3 was developed by the authors of this report by computing a distribution for the skewness coefficient for $10,000$ samples of the given size from a normal distribution with mean-zero and variance-one. Values from Snedecor and Cochran (1967) for sample sizes of 25 and 30 are included for comparison. The difference is negligible at $n=25$ and is approximately $1\ 1/2\%$ at $n=30$.

Table 5.2 Definition of Tests Studied

<u>Name</u>	<u>Code Name</u>	<u>Description</u>	<u>Reference</u>
Shapiro-Wilk	W	$W = \frac{\left[\sum_{i=1}^{[n/2]} a_{n-i+1} (y_{n-2i+1} - y_i) \right]^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$ <p>where $[n/2]$=greatest integer in $n/2$ a_{n-i+1}=coeff. tabulated in Shapiro-Wilk (1965)</p>	Shapiro et al. (1968)
Skewness coefficient	$\sqrt{b_1}$	$\sqrt{b_1} = \sqrt{n} \frac{\sum_{i=1}^n (y_i - \bar{y})^3}{\left[\sum_{i=1}^n (y_i - \bar{y})^2 \right]^{3/2}}$ <p>where y_i=ith observation</p> $\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i \quad n=\text{number of observations}$	Snedecor and Cochran, 1967
Kolmogorov-Smirnov	KS	$KS = \max \left \frac{i}{n} - F(y_i) \right \quad i=1, 2, \dots, n$ <p>where $F(\cdot)$ is the hypothesized cdf</p>	
Chi-squared (equiprobable cells)	CS	$CS = \frac{k}{n} \sum_{i=1}^k C_i^2 - n$ <p>where k=number of cells c_i=number of observations per cell</p>	

Power against Chi Square

X² (4)

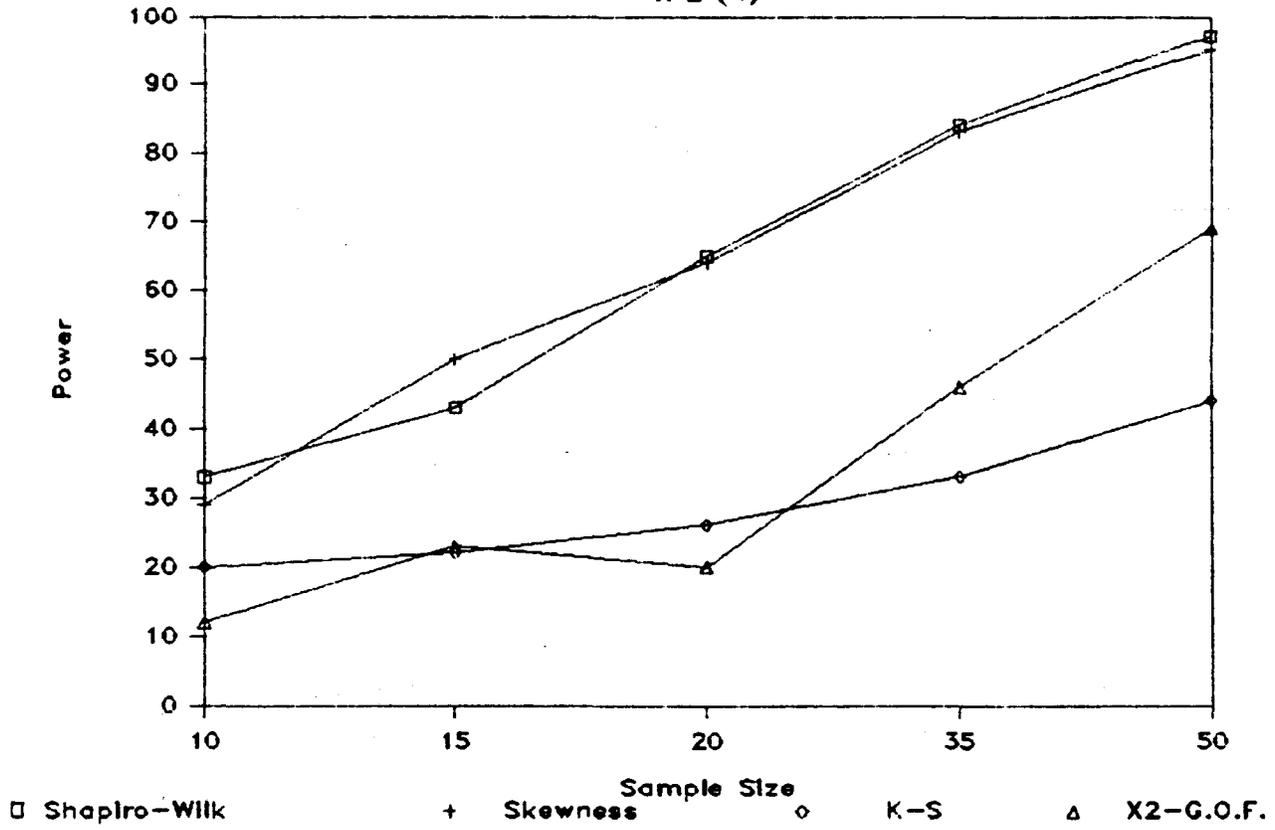


Figure 5.1 Power of tests to detect non-normality against an alternative of chi-squared with 4 degrees of freedom. The tests are the Shapiro-Wilk statistic, skewness coefficient, Kolmogorov-Smirnov statistic and chi-squared goodness of fit test. Data are from Shapiro et al. (1968).

Power against Chi Square

$\chi^2(10)$

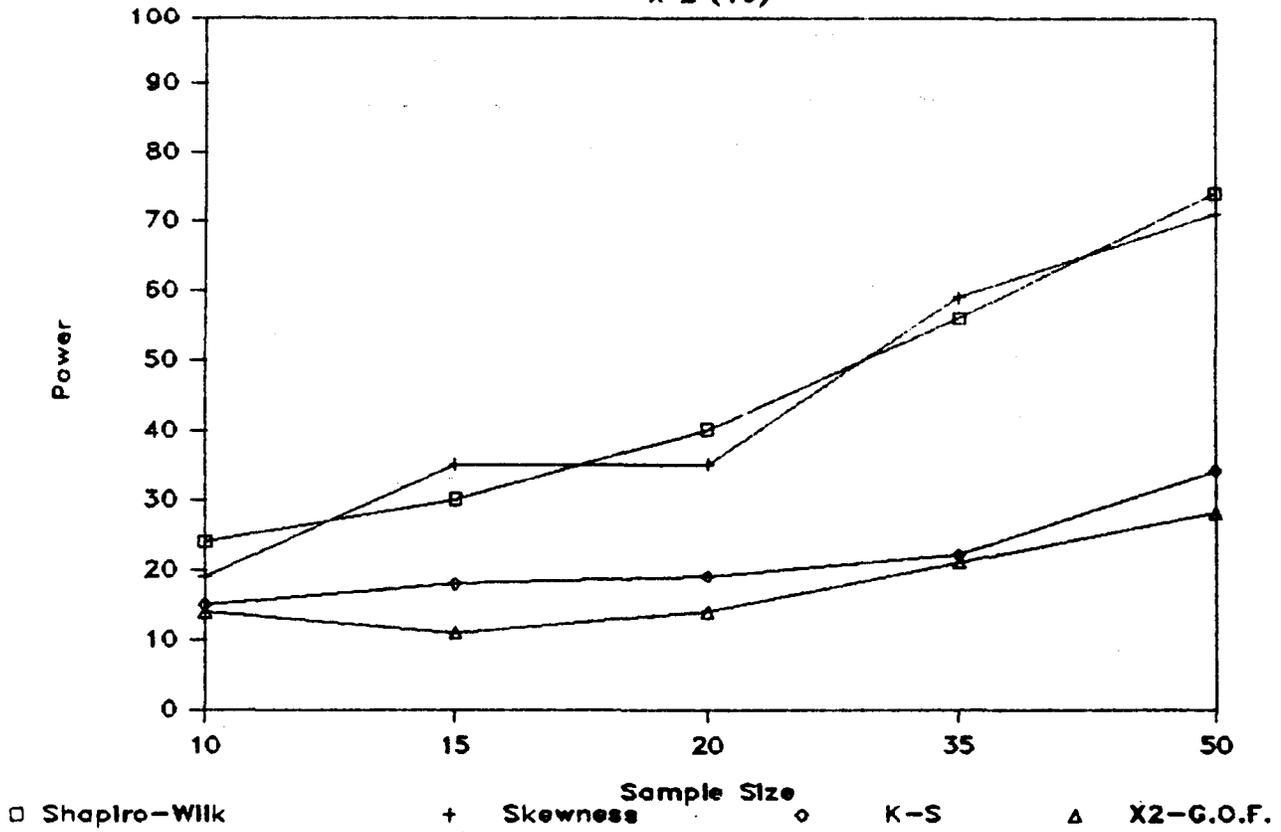


Figure 5.2 Power of tests to detect non-normality against an alternative of chi-squared with 10 degrees of freedom. Data are from Shapiro et al. (1968).

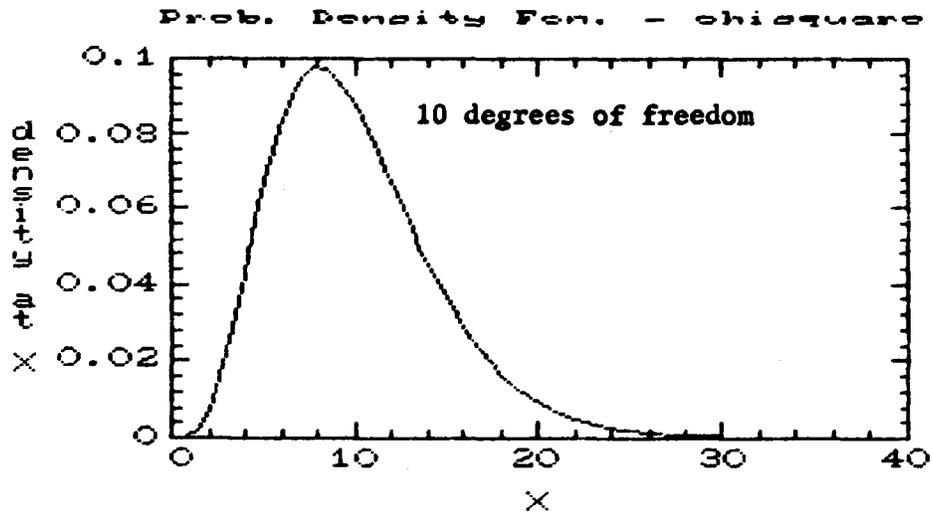
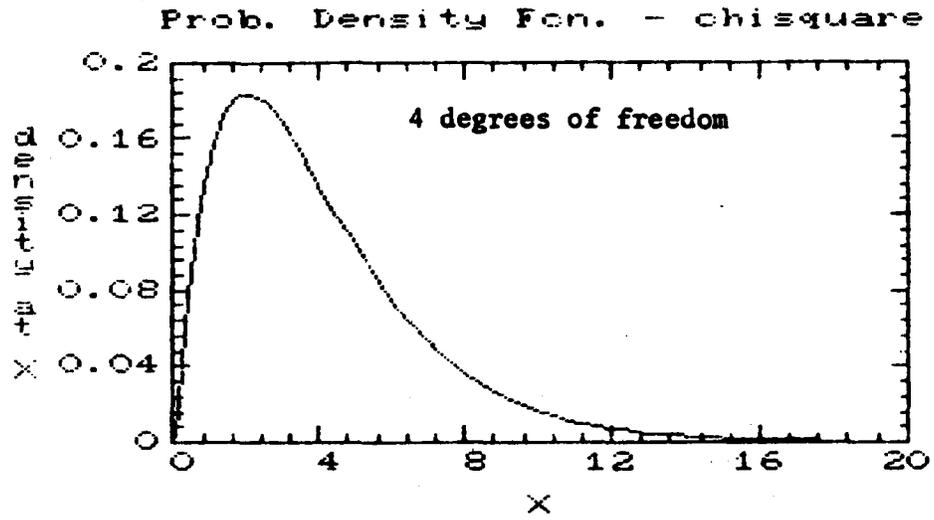


Figure 5.3 Probability density functions for a chi-squared random variable with 4 and 10 degrees of freedom.

Table 5.3. Values of the skewness coefficient at 5% and 1% significance levels obtained by Monte Carlo simulation. Values in parentheses are from Snedecor and Cochran (1967).

<u>Sample Size</u>			
<u>n</u>	<u>$\sigma=.05$</u>	<u>$\sigma=.01$</u>	<u>Standard Deviation</u>
9	0.953	1.420	0.592
10	0.950	1.395	0.582
11	0.927	1.358	0.565
12	0.915	1.331	0.553
13	0.886	1.306	0.539
14	0.861	1.291	0.529
15	0.854	1.280	0.522
16	0.833	1.246	0.511
17	0.817	1.220	0.496
18	0.798	1.197	0.489
19	0.769	1.161	0.476
20	0.777	1.146	0.473
21	0.753	1.116	0.463
22	0.742	1.099	0.455
23	0.732	1.087	0.446
24	0.710	1.074	0.437
25	0.712 (0.711)	1.060 (1.061)	0.437 (0.4354)
26	0.689	1.013	0.421
27	0.689	1.016	0.419
28	0.674	1.006	0.413
29	0.669	0.992	0.408
30	0.651 (0.662)	0.972 (0.986)	0.400 (0.405)

The power of the test to distinguish between a normal distribution and the chi-square distribution with 10 degrees of freedom, $\chi^2(10)$, is not very high. The standardized third moment of the $\chi^2(10)$ is 0.89 compared to 0 for the normal distribution. The third moment can provide a measure of the symmetry of the distribution with zero indicating perfect symmetry. By comparison, the $\chi^2(4)$ shown in Figure 5.3 has a standardized third moment of 1.41. The power of the skewness coefficient to detect non-normality in the form of a $\chi^2(10)$ distribution is only 0.35 for a sample size of 20 or 5 years of quarterly samples. After 50 samples or 12 1/2 years, the test would detect non-normality with a probability of 0.71.

IV. Testing for Serial Correlation

In the absence of seasonality, the only type of dependence structure considered in this study is serial correlation. Based on the results of Chapter Four, one might conclude that quarterly ground water quality data are often independent if they are not seasonal. However, conclusions regarding serial dependence are even more difficult to draw than those regarding seasonality and normality.

Serial correlation is expressed by the autocorrelation coefficient, the covariance of observations separated by a number of time intervals divided by the variance of the process. The selected number of time intervals is the lag. In the present study which focuses on quarterly ground water quality data, only lag-one autocorrelation is considered.

The distribution of the sample autocorrelation coefficient for lag-one, $r(1)$, is necessary to construct confidence intervals. While the exact distribution is not known, Bartlett's Formula allows an approximation for a given or assumed model (Marriot and Pope, 1949). Because this is an asymptotic result, it gives a lower bound on the estimate of variance. For a white noise (uncorrelated) process, the sample autocorrelation coefficient for lag-one is distributed approximately asymptotically normal with zero mean and variance of $1/n$. The 95% confidence interval on $\rho(1)$ is $\pm 1.96(n)^{-1/2}$ for an uncorrelated process. Figure 5.4 shows half the confidence interval as a function of sample size. For small values of n , the confidence interval includes essentially the entire range of possible values of $r(1)$, from -1 to +1. Even after 20 observations or 5 years of quarterly samples, the confidence interval is ± 0.44 . Any lag-one sample autocorrelation coefficient calculated with 20 observations will be assumed to be zero if it is less than ± 0.44 .

For an AR(1) process, the serial correlation at lag-one is nonzero. The approximate distribution of $r(1)$ is asymptotically normal

$r(1)$ - confidence interval

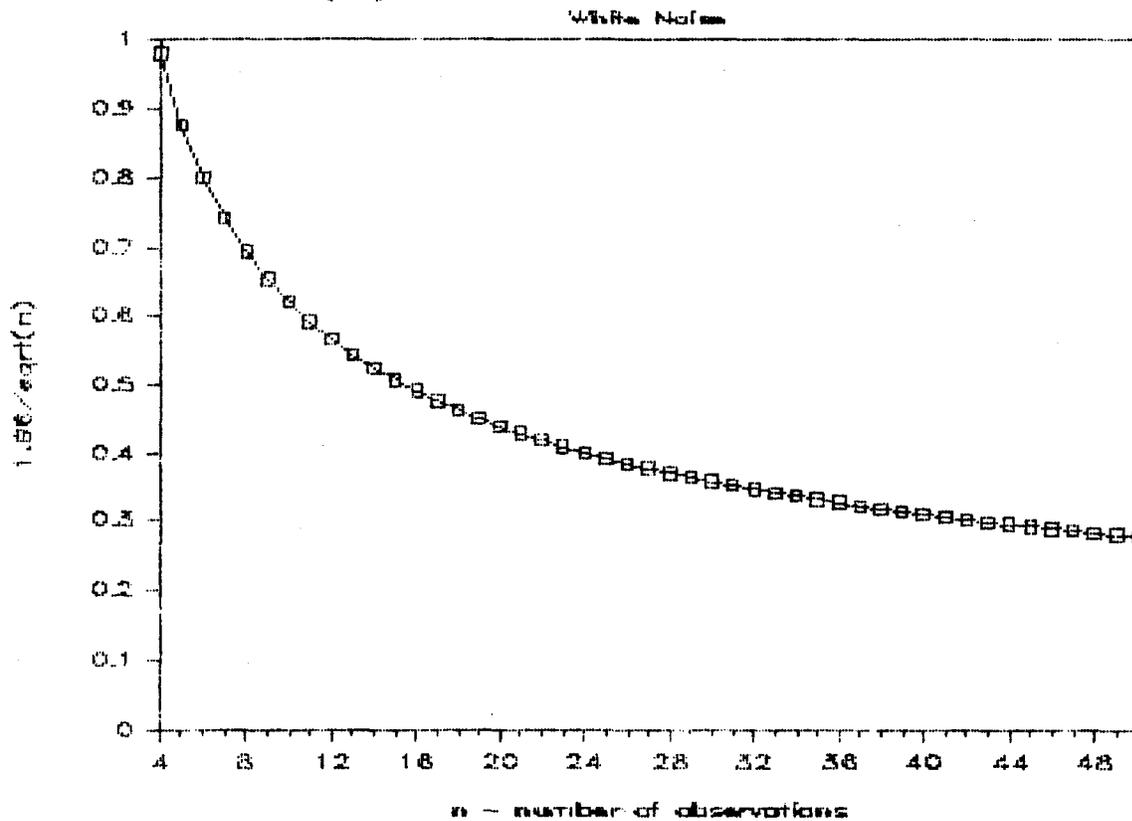


Figure 5.4 One half of the confidence interval (95%) width for the sample autocorrelation coefficient of white noise.

with mean equal to the actual value of the autocorrelation coefficient, $\rho(1)$, and variance equal to $(1-\rho(1)^2)/n$. The 95% confidence interval on $\rho(1)$ is $r(1) \pm 1.96[(1-\rho(1)^2)/n]^{\frac{1}{2}}$. This form is similar to that of the white noise process, and the width of the confidence interval for an AR(1) process is related to the corresponding white noise confidence interval by a factor of $(1-\rho(1)^2)^{\frac{1}{2}}$. As the amount of serial correlation increases, the width of the confidence interval decreases.

For moderate levels of correlation, there is considerable overlap in the confidence intervals of white noise processes and AR(1) processes. It is, therefore, very difficult to distinguish the two with small to moderate sample sizes. For example, if $\rho(1)=0.4$, the variance of $r(1)$ for $n=20$ is $(1-0.4^2)/20 = 0.042$. To compute the power of detecting significant correlation of the AR(1) type, one proceeds as follows. The probability that a sample value of $r(1)$ will be large enough to reject the null hypothesis (that the series is uncorrelated) is equal to the probability that $r(1)$ will exceed the upper 95% confidence limit for $\rho(1)$ of a white noise process or 0.44. Assuming a normal distribution, this probability is 0.424. That is, if the process is actually AR(1) with $\rho(1)=0.4$, the probability of concluding that the process is not uncorrelated after 20 observations is 0.42. After 40 observations, the probability is 0.73.

Roughly speaking therefore, it is not likely that moderate amounts of serial correlation can be detected in quarterly ground water data without at least 10 years of data.

V. Conclusions Regarding Tests for Characterizing Ground Water Quality Variables

The following conclusions can be stated regarding statistical characterization of ground water quality.

The Student's t-test is appropriate to test for differences in seasonal means when there is reason to believe that one season is different from the others and the data are not skewed. For skewed data, the Mann-Whitney distribution-free test can be applied.

If there is no evidence to distinguish one season from the others, the analysis of variance (ANOVA) test is appropriate for normal or symmetric data. The Kruskal-Wallis distribution-free test should be used for skewed data.

The asymptotic relative efficiency of the Mann-Whitney test to the t-test is 0.955 when the assumptions of the t-test are met. The ANOVA and Kruskal-Wallis are k-sample extensions of two-sample counterparts

and have the same asymptotic relative efficiency of the distribution-free test to the normal theory test. If there is doubt as to whether observations come from a normal population, the distribution-free tests should be used. There is very little efficiency lost.

The skewness coefficient is the most powerful test for normality against a skewed alternative. Even so, its power is not great against a distribution that is only moderately skewed. The example presented was a $\chi^2(10)$ distribution with a standardized third moment of 0.89. The power of the skewness coefficient to detect non-normality was given as 0.35 after 20 samples.

Serial correlation will be very difficult to determine with precision. Small sample sizes are associated with large confidence intervals. Moderate amounts of dependence will often be obscured. The probability of detecting dependence of $\rho(1)=0.4$ after 20 samples is 0.42.

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CHAPTER FIVE

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CHAPTER SIX

STATISTICAL METHODS FOR DETECTING CHANGES IN GROUND WATER QUALITY

I. Introduction

Attention now turns to the issue of trend detection. In the early years of a regulatory monitoring program, the characteristics of the pertinent variables cannot be determined precisely. Therefore, the selection of statistical tests for detecting changes in quality will be somewhat subjective. However, one can minimize the chances of making very poor choices by relying most heavily on statistical tests which are comparatively insensitive to initial assumptions on seasonality and normality.

Unfortunately, the effect of serial dependence is significant for virtually all statistical tests of hypotheses which might be used in regulatory monitoring. Since insufficient data are currently available to characterize the correlation structure of water quality random variables, the logical approach is probably to assume initially that quarterly samples are uncorrelated when they are not seasonal. One should also keep in mind that all of the tests described in the following discussion perform less satisfactorily if serial correlation is present than if they are used with independent samples.

This chapter begins with a discussion of methods which are currently used or proposed for detecting changes (trends) in regulatory monitoring programs. The limitations of current methods are presented in light of the information contained in previous chapters. The latter part of the chapter suggests new approaches for overcoming these limitations. The chapter closes with a discussion of the question of nondetects.

II. Current Approaches to Regulatory Data Analysis

The regulations associated with RCRA currently require a detection monitoring program in which ground water quality data are to be collected at least quarterly from upgradient wells for one year for four indicator variables (pH, total organic carbon, specific conductance, and total organic halogens) in order to establish background conditions. After the first year, both upgradient and downgradient wells are sampled at least semiannually and statistically compared with background data to detect significant changes. Statistically significant

degradation of downgradient water quality results in the implementation of a more involved compliance monitoring program which would lead to a clean-up effort.

The required sampling frequency and statistical analysis procedures for detection monitoring are spelled out in the regulations. Since RCRA has gone beyond other legislative efforts to standardize monitoring and data analysis procedures, it has received much attention and criticism regarding the appropriateness of the specified approach. In particular, serious questions have been raised regarding the choice of the hypothesis test which is specified in the regulations and the specification of sample size based on replicate analyses.

A specified test for comparison of means in ground water quality is Cochran's Approximation to the Behrens-Fisher Student's t-test. Although current recommendations from EPA include this test as only one of several possible approaches, the current discussion will focus on this test as representative of currently recommended methodology. This test was developed for the comparison of means from two populations in which the variances are not necessarily equal. (The usual t-test assumes that the two variances are equal.) The assumptions of the specified test are that the two populations are normally distributed and that the samples are independent.

The problem of testing for equality of means when the variances are unequal is referred to as the "Behrens-Fisher Problem." The associated hypothesis test requires the use of special tables. However, for Cochran's Approximation, which is employed in practice, regular t-tables may be used. Although there is some error involved in the approximation, other limitations of this approach, as described below, are probably more significant.

The first limitation is the normality assumption. Many water quality random variables are clearly not normal, particularly if there is significant fraction of nondetects in the data record. EPA has recognized the problem of non-normality in the past and at one time recommended a nonparametric approach, the Mann-Whitney test. Currently, EPA suggests that if the coefficient of variation of sample data is less than 1.0, the data may be regarded as normal for the purpose of the tests. This assumption is questionable. As indicated in Chapter Five, a skewness test would be much preferred. In the absence of normality, other "equivalent" tests may be utilized if approved by EPA.

The second limitation is the assumption of independence. As long as samples are taken quarterly or less frequently, an assumption of serial independence is probably justified. However, the presence of predictable seasonal variation is still likely. Quarterly sampling to

establish background concentration values is purported to account for seasonal variation, but the statistical test, as written into the regulations, is inappropriate for the analysis of seasonal data.

Supposedly, the use of a test which does not require equal population variances addresses this issue since the background data would include seasonal variation and subsequent data sets might not. This is not a very sound argument statistically, however, and brings up the third limitation, which is the question of whether the assumption of unequal variances is appropriate. In most cases, it would seem that such an assumption is not appropriate since under the null hypothesis (that the two means are equal) one infers that no change has occurred. One would, therefore, expect the variances to be equal as well as means.

The fourth limitation is the question of how the sample size should be specified for the test. EPA has in the past stated that if four quarterly samples are taken and four replicate analyses are performed on each, the sample size is 16. This is a rather serious error since one does not have 16 independent samples. The correct approach is to average the replicates and use a sample size of four. The effect of using a sample size of 16 is to greatly increase the probability of a Type I error, false detection of a change.

This brings us to the fifth limitation, which is the specification of the Type I error or significance level for the test. EPA originally specified a significance level of 0.05 and has since retreated to 0.01. If the test were properly constructed and all assumptions satisfied, this would probably be too low and would provide inadequate power or ability to detect degradation of water quality. Because of the discussed questions regarding normality, seasonality, and sample size above, however, the actual significance level of the test may be much different from 0.01 (probably larger). In fact, there is no way to tell what it really is.

Since EPA's recommended procedures have, in the past, failed to account for much of the variation in ground water quality data, much of the current ground water literature has been aimed at discussions of the statistical aspects of ground water and the deficiencies of RCRA regulations.

The statistics of ground water quality, in general, were examined by Nelson and Ward (1981) who discuss sampling frequency in relation to spatial and serial correlation. They also describe sampling techniques appropriate to various situations.

Sgambat and Stedinger (1981) also discuss the statistics of ground water quality. They point out that concentrations of ground water

constituents are highly variable, and this variability affects data interpretations. Trends in ground water quality can be erroneously interpreted as resulting from man's activities unless the data record is "reasonably long." They also discuss the relation between sampling frequency and the probability of a well violating drinking-water standards. If each sample has a 10% chance of violating the standard, the probability that the standard will be violated during a year when monthly samples are taken is 0.72.

Rovers and McBean published a series of articles in which they discussed individual aspects of ground water quality statistics. The Mann-Whitney distribution-free test was compared to the Student's t-test for detecting differences in means (Rovers and McBean, 1981). The authors suggested transforming the data to eliminate differences in the variance of two samples in the t-test. They felt the t-test was superior for small samples, since the information contained in the magnitude of sample values was lost when the values were ranked for the Mann-Whitney test.

Later, (McBean and Rovers, 1984b) the same authors presented regression analysis as an alternative to the t-test to determine whether or not a trend exists. They recommended dividing the data series into two parts and testing to see if the least squares best fit lines of the parts were different from each other. Another alternative method was suggested where a line is fit to the entire series and tested to determine if its slope is different from zero. Another article (McBean and Rovers, 1984a) gives alternatives for assigning values to constituents below detection levels. Finally, in an article aimed specifically at RCRA regulations, McBean and Rovers (1985), illustrated that the variance associated with successive samples can be much than that associated with replicates from the same sample. Therefore, replicates should not be used as a substitute for successive sampling.

Zar (1982) discussed the power of the t-test, i.e. the probability the null hypothesis will be rejected when it is, in fact, false. He explained the relation of the sample size to power and noted that the power could be increased by increasing the number of samples. Power is also increased by raising the significance level, but this also increases the probability of incorrectly rejecting the null hypothesis.

III. Paired Well Approach

The previously suggested approaches to statistical analysis of ground water quality data generally involve the comparison of individual observations or sample means of water quality from wells affected by (downgradient of) the regulated facility to average values of

background or unaffected water quality. Background water quality may be determined by sampling wells upgradient of the facility, in which case the comparison described above is made across space. Alternatively, background water quality may be determined by sampling prior to the operation of a facility, in which case the comparison is made across time.

Neither approach can reliably accomplish the stated objective of monitoring. First, because naturally occurring spatial variability in ground water quality, we cannot be sure that upgradient wells adequately characterize background conditions of water quality. There are many situations where water quality under natural conditions gets better or worse as the sampling location moves downgradient. Differences in water quality between upgradient and downgradient wells cannot generally be assumed to result from a facility in between.

Second, the time period available for sampling prior to operation of a facility is usually short, typically one to two years or less. This length of time is inadequate to characterize background water quality and provide a baseline for comparisons of water quality over time (Sgambat and Stedinger, 1981). Furthermore, an apparent trend in water quality at a downgradient well could only be assumed to result from a regulated facility if one could show with confidence that the same trend did not exist in upgradient wells.

A simple way to overcome these difficulties is to use paired observations between upgradient and downgradient wells. One treats the difference between an upgradient (unaffected) observation and a downgradient (affected) observation, collected at roughly the same point in time, as a single observation. One could reasonably assume that both upgradient and downgradient wells are equally affected by seasonal effects and water quality impacts other than those caused by the regulated facility, while the facility impacts only the downgradient well. If these assumptions hold and if sampling is begun at a point in time at which no pollution has yet occurred, the stated objective of monitoring can be accomplished through statistical tests for a shift in the level of the differences. If pollution has already occurred at the downgradient well, a shift in the level of differences would indicate either further degradation or improvement in water quality at the downgradient well, relative to the upgradient well. Thus, pairing of observations can be used to evaluate the effectiveness of clean-up efforts.

If more than one upgradient well is used, the observations could be averaged over space, if desired, to provide a single observation prior to pairing with downgradient observations. However, each downgradient observation should be paired individually with the upgradient mean, since pollution could easily occur in only one downgradient well.

Replicate chemical analyses on a given sample should, of course, be averaged to provide a single sample. The replicates are not independent and should not be treated as separate observations.

There is generally a "price" associated with data transformations to meet the required assumptions for statistical analyses. The present case is no exception. By pairing observations, one overcomes the difficulties associated with making comparisons only over space or only over time. However, the sample size is reduced by half. Likewise, averaging of replicate analyses reduces the sample size but preserves independence of samples and reduces the laboratory analysis variance.

IV. Testing for Shifts in Level

Once the paired observation approach has been adopted, one may use a variety of statistical tests of hypotheses to check for shifts in the level of the differences. Two well-known approaches are discussed here for the purpose of illustrating the paired well concept and for demonstrating the difficulty of detecting small shifts in quality over relatively short time frames. The first approach is to examine each difference as the data are collected using statistical tolerance intervals. If the observation (difference) falls inside the tolerance interval, one concludes that no significant shift in level has occurred. If the observation falls outside the interval, one concludes that a shift has occurred, i.e. one well has been impacted compared to the other. This approach is best suited for detecting large impacts which occur over a short time frame.

The second approach is to examine a sequence of observations (differences) for trend, using an appropriate test of hypothesis. This approach is better suited for detecting slowly evolving changes in water quality. In this approach, one must decide a priori where the trend starts, usually through visual inspection of a time series plot.

Both the tolerance interval and trend test approaches will be discussed in some detail in the following sections. Nonparametric approaches will be included to handle situations where the data are not normally distributed. The problem of serial correlation will be sidestepped for the present by limiting the discussion to the case of quarterly sampling, the frequency currently specified in RCRA regulations. The authors have found that quarterly samples are generally uncorrelated, based on their analysis of ground water quality data from case study states.

V. Statistical Tolerance Limits: normally distributed data

Statistical tolerance limits define an interval such that there is a certain probability $(1-\alpha)$ that a certain fraction (q) of a given distribution will be contained in the interval. Such intervals may be obtained in a variety of ways and are not unique. The present discussion will show how such intervals may be obtained for a set of water quality observations when the underlying distribution is either normal or unspecified.

For the normal case, the form of the interval is

$$\bar{X} \pm K S$$

where

\bar{X} - sample mean of observations

S - sample standard deviation of observations

(6.1)

The factors K are tabulated (see Bowker and Lieberman, 1972) for both one-sided and two-sided intervals and several values of α and q . To compute the desired tolerance limits, therefore, one need only compute the sample standard deviation from a set of observations and look up K corresponding to the sample size n and the desired values of α and q . A derivation of tolerance limits for the normal distribution is presented in Hald (1952).

For small sample sizes, the tolerance interval will be wide; therefore, a large shift in water quality levels would be required for an observation to fall outside the tolerance limits. As more data become available, the tolerance interval will become narrower, and the test will become more sensitive to smaller shifts in water quality.

As an example, consider the following quarterly sulfate concentration data which were collected over a two-year period beginning in 1981 at the Rocky Mountain Arsenal near Denver, Colorado. (See Table 6.1)

For the purposes of this discussion, assume that these data represent the status quo. Tolerance limits are to be used to determine whether future observations, considered one at a time, represent a significant improvement or degradation of water quality in the down-gradient well relative to the upgradient well. The sample mean of the eight quarterly differences is 27 mg/l and the sample standard deviation is 18.1 mg/l. Using Table 8.3 of Bowker and Lieberman (1972) one can obtain the factor K in equation (1) for given values of $1-\alpha$ and q and write the corresponding tolerance limits. Suppose that $1-\alpha=0.95$

Table 6.1 Example Data

Quarter	Downgradient Well SO4 mg/l	Upgradient Well SO4 mg/l	Difference mg/l
1	72	57	15
2	89	70	19
3	91	50	41
4	90	49	41
5	94	69	25
6	74	51	23
7	68	71	-3
8	85	30	55

and $q=0.9$, i.e. the stated tolerance interval contains 90% of the population at a confidence level of 95%. The tolerance limits are

$$\bar{X} \pm K S$$

$$17.0 \pm (3.163)(18.1)$$

$$17.0 \pm 57.3 \text{ mg/l}$$

The tolerance interval is then -30.3 to 84.3 mg/l. Unfortunately, since this interval is rather wide, it will be relatively insensitive to small changes in future water quality. Suppose that the future samples are a repeat of the past eight except that a step change of 30 mg/l is added to each downgradient sample. Then, exactly one observed difference will fall outside the tolerance interval. A smaller step change would not be detected.

Suppose now that one wishes to be more "certain" of any conclusions that a change has occurred by reducing the chance of an observation falling outside the tolerance interval when no change had actually occurred, i.e. by reducing the Type I error.

This can be accomplished by increasing $1-\alpha$ to 0.99 and q to 0.99. In this case $K=6.468$, and the resulting tolerance interval is -90.1 to 144.0 mg/l. This interval will be much less sensitive to changes than the first, illustrating the penalty, loss of sensitivity or power, which is associated with increased confidence in conclusions that changes have occurred.

Of course, as the sample size increases, the tolerance interval will become narrower. For example if $n=16$, one finds $K=2.437$ and 4.492 respectively for the values of $1-\alpha$ and q considered above. Tolerance intervals will also be narrower if the standard deviation decreases. As mentioned earlier, ground water quality data tend to be characterized by a high degree of variability; however, the total variance can be reduced by minimizing laboratory analysis error and sampling error. Reduction of error is, therefore, accompanied by an increase in ability to detect changes in water quality.

VI. Statistical Tolerance Limits: nonparametric

Distribution-free tolerance limits may also be obtained which do not depend on an assumption of normality. Since many ground water quality random variables are not normally distributed, this is a significant advantage. Distribution-free tolerance intervals are, however, wider and therefore less sensitive to changes in water quality

than their normal counterparts. Distribution-free tolerance limits are discussed thoroughly in Conover (1980). Their derivation is based on order statistics; therefore, the limits will correspond to observed sample values.

The m th order statistic, $X(m)$, is defined as the m th smallest of a set of n observations, i.e. $X(1)$ is the smallest observation $X(2)$ is the next smallest, . . . , and $X(n)$ is the largest observation. A distribution-free tolerance interval consists of an interval from $X(r)$ to $X(n+1-m)$ inclusive such that there is a probability of $1-\alpha$ that a proportion q of the population is contained in the interval. Our task is to find r and m for a given n . For special situations, such as $r+m=1$ or $r+m=2$, tables are included in Conover (1980) which provide n directly. The case $r+m=1$ corresponds to a one-sided interval where the tolerance limit is the largest or smallest observation. The case $r+m=2$ corresponds to a two-sided interval bounded by the largest and smallest observations. For other situations, the following approximation is suggested.

$$n = \frac{1}{4} \chi^2_{1-\alpha} \frac{1+q}{1-q} + \frac{1}{2} (r + m - 1) \quad (6.2)$$

where

$\chi^2_{1-\alpha}$ is the $1-\alpha$ quantile of a chi-square random variable with $2(r + m)$ degrees of freedom

n = required sample size

q = proportion of distribution contained within the tolerance interval at a confidence level of $1-\alpha$.

Using this relationship, one-sided intervals may be obtained by setting either r or m equal to zero and solving for the other for a given n by trial and error. For two-sided intervals, there would be more than one combination of r and m which would provide a valid tolerance interval for given values of α and q . A two-sided interval would be used when one is looking for either improvement or degradation in water quality while a one-sided interval would be appropriate when one is looking only for improvement or only for degradation.

Now, return to the example data set considered earlier. Referring to Table A6 of Conover (1980), the "best" one can do in terms of a two-sided nonparametric tolerance interval with eight data points is $1-\alpha=0.7$ and $q=0.7$. In this case, the upper tolerance limit is the largest observation while the lower tolerance limit is the smallest observation. Thus, for the example data, the tolerance interval is -3 to 55 mg/l. For comparison, a two-sided tolerance interval based on the normal distribution for $1-\alpha=0.75$ and $q=0.75$ is $X \pm 1.568S$ or -1.3 to

55mg/l. Thus, if one can assume that the distribution is normal, one can state that the same interval would contain a larger proportion of the population at a higher level of confidence.

An upper one-sided tolerance limit is formed by the largest observation for $1-\alpha=0.80$ and $q=0.80$.

Significantly increasing $1-\alpha$ and/or q requires large increases in the number of observations. For example, to form a two-sided tolerance interval for $1-\alpha=0.95$ and $q=0.90$ would require 72 observations while an interval for $1-\alpha=0.99$ and $q=0.99$ would require 662 observations or 165 years of quarterly data.

VII. Trend Tests

To detect gradual changes, one should examine a sequence of observations for trend rather than consider observations individually. If normality can be assumed, one can simply fit a linear regression line to a plot of the observations versus time. A t-test is then used to determine whether the slope is significantly different from zero. The test may be either one-sided or two-sided. A significant slope indicates that a significant trend is present. Any basic statistics text, for example, Snedecor and Cochran (1967) or Bowker and Lieberman (1972), can be consulted for the methodology. McBean and Rovers (1984b) illustrate regression modeling with ground water quality data. Furthermore, most statistical packages for mainframes and microcomputers have this capability. Therefore, the details will be omitted here.

The implications of a small sample size can be evaluated by calculating the power of the t-test for various sample sizes and trend magnitudes. The power ($1-\beta$) of the test is the probability of detecting a trend given that one exists. The probability of not detecting a trend given that one exists is β , called the Type II error. (As mentioned earlier, the Type I error is the probability of concluding that a trend is present when one does not exist.)

Lettenmeier (1976) presents a simple approach to calculating the power of the t-test. First, one computes the dimensionless trend number N_t' from

$$N_t' = \frac{[n(n+1)(n-1)]^{1/2} \tau}{(12)^{1/2} \sigma} \quad (6.3)$$

where

n - number of samples used in the regression

τ - trend magnitude in units per sampling interval

σ - standard deviation of the random process in the absence of a trend

Then the power of the test is given by $1 - \beta = F(N_t - t_{1-\alpha/2, \nu})$ (6.4)

where F is the cumulative distribution function of the Student "t" distribution with degrees of freedom $\nu = n - 2$.

Table 6.2 shows the power of trend detection for a range of sample sizes from $n=4$ to 24, significance levels of $\alpha=0.20$ and $\alpha=0.05$, and trend to standard deviation ratios, τ/σ , of 0.05, 0.2 and 0.5. Returning to the previous example where $n=8$ and assuming that $\sigma=S=18.1$, one observes that a trend magnitude of 0.905 mg/l per quarter ($\tau/\sigma=0.05$) or 3.62 mg/l per year would be detected with a probability of 0.15 at a significance level of 0.20. To achieve a power of 0.81 for the same trend magnitude and significance level would require a sample size of 28 or 7 years of data, at the end of which the total relative change in sulfate concentration between the two wells would be 25.3 mg/l. On the other hand, a trend of 9.05 mg/l per quarter ($\tau/\sigma=0.5$) would be detected with a probability of .94 based on a sample size of 8 and $\alpha=0.20$. Such a trend is so large, however, that its presence would be apparent by inspection. The power of trend detection is, of course, even worse at a significance level of 0.05. Thus, one must realize that small to moderate trends are not detectable (in the presence of moderate error or noise) with small numbers of data.

If an assumption of normality is not reasonable, one can apply a nonparametric test for trend, for example Spearman's rho or Kendall's tau (Conover, 1980). These tests are almost as powerful as the t-test for data which are normally distributed, and will generally perform better when the data are not well described by the normal distribution. Furthermore, most statistical packages for microcomputers and mainframes can easily perform these tests. However, the difficulty of detecting trends of small or moderate magnitude in a short time frame will be of concern whether normal or nonparametric methods are used.

One might assume that the solution would be to collect samples on a more frequent basis, for example monthly. Monthly sampling would provide additional information; however, more frequent sampling could result in serial correlation of observations (redundancy in information between samples). Therefore, less information would be obtained per observation than if the samples were spaced farther apart and were independent.

Table 6.2 Power, $1-\beta$, of trend detection for t-test

n \ τ/σ	$\alpha = 0.20$			$\alpha = 0.05$		
	0.05	0.20	0.50	0.05	0.20	0.50
4	0.11	0.14	0.26	0.03	0.03	0.04
8	0.15	0.45	0.94	0.04	0.15	0.77
12	0.23	0.83	1.00	0.07	0.56	1.00
16	0.34	0.98	1.00	0.12	0.93	1.00
20	0.50	1.00	1.00	0.22	1.00	1.00
24	0.64	1.00	1.00	0.35	1.00	1.00
28	0.81	1.00	1.00	0.53	1.00	1.00

Selection of sampling intervals when observations are serially correlated is discussed in Lettenmaier (1976) and Loftis and Ward (1980) for surface water quality monitoring. Extension of the work to ground water quality monitoring is somewhat difficult because sample sizes are often too small to adequately characterize the correlation structure of the data. This topic, therefore, remains as one for future research.

VIII. Conclusions Regarding Testing for Changes in Water Quality

The primary objective of regulatory ground water quality monitoring is the detection of adverse changes in ground water quality caused by a specific facility. The pairing of water quality observations between upgradient and downgradient wells is suggested as an improved approach to monitoring data analysis for the stated objective. The resulting differences may be examined by a variety of techniques to detect shifts in level along with their implied water quality impacts from a facility.

Two such approaches, statistical tolerance limits and trend testing, were discussed as examples of how paired observations might be utilized for the regulatory objective. Tolerance limits are appropriate for detecting abrupt changes on a sample-by-sample basis while trend tests are appropriate for detecting gradual changes over longer time periods. In both approaches, the statistical tests may be either one-sided or two-sided and may be either based on a normality assumption or nonparametric.

It was shown that neither approach is capable of detecting small changes with a small number of samples. Thus, for quarterly sampling, several years of data are needed before meaningful conclusions can be drawn.

IX. Interpreting Nondetects

Many water quality records contain large numbers of zeros "less than," and "nondetects"--all of which mean that the measured concentration was below the method detection limit (MDL). This situation is especially frequent for trace elements and toxic constituents, some of which are considered to be significant at concentrations near the detection limit. All three types of entries, henceforth referred to as nondetects, create significant problems in data analysis such as calculation of means or testing for trends. These problems exist because it is impossible to associate a definite numerical value with a nondetect. All one knows is that the observed signal in laboratory analysis was less than that of the method detection limit and, therefore,

that the actual concentration was most likely less than the reported detection limit concentration. The latter is not absolutely certain. A single sample containing analyte at exactly the MDL concentration has a 50% probability of being reported as a nondetect and a 50% probability of being reported at a detectable concentration.

One of the major difficulties in interpreting and utilizing nondetect data is that data users often do not understand the meaning of an observation recorded as a nondetect. This is understandable since there are several approaches to computing the method detection limit which can result in widely disparate values. The MDL is really a fixed value of the signal from an analytical device, such as an atomic absorption unit, below which the analytical chemist has little confidence in the numerical accuracy of the results. In other words, the signal-to-noise ratio is "too small for comfort." Obviously, the exact value the MDL should take is somewhat subjective. Thus, a few "standard" approaches to setting the MDL have been adopted. Two common approaches, the IUPAC method and the EPA method, will be briefly described below. Before discussing these specific procedures, let us present a general and qualitative definition of MDL as "the smallest concentration of a given substance which can be detected by a given analytical procedure." Both the International Union of Pure and Applied Chemistry (IUPAC) and EPA recognize the significance of uncertainty in analytical measurements in their procedures for finding the MDL; therefore, the procedures are given in statistical terms.

The IUPAC approach to finding the MDL (Winefordner and Long, 1983) is based on achieving a high probability that a sample which does not contain the analyte of interest will be measured and recorded as a nondetect. Specifically, the IUPAC MDL is the concentration which corresponds to a nonexceedence probability of 99.87%, based on the analysis of blank samples. That is, if 10,000 blanks were analyzed for the particular substance, one would expect only 13 of them to show concentrations greater than the MDL.

The MDL is found by analyzing a "large" number of blanks using the specified analytical equipment, procedure, and matrix in which the analyte would be found. The standard deviation of the blank signals σ_B is then estimated as the sample standard deviation S_B . Then the MDL is calculated from

$$\text{MDL} = 3S_B/k \quad (6.5)$$

where k is the slope of the concentration versus signal function. S_B/k will therefore be in concentration units as will the MDL. Assuming that the blank signals, which may be thought of as errors or noise,

are normally distributed and that S_B accurately estimates σ_B , there is a 99.87% probability that a given blank measurement will not exceed the MDL.

The EPA method (Glaser et al., 1981), on the other hand, is based on achieving a high probability that a sample which does contain analyte at a concentration above the MDL will result in a measurement greater than zero. Specifically, the EPA MDL is the concentration for which the probability of obtaining a blank-corrected signal greater than zero is 99%. Thus, out of 10,000 samples containing analyte at the MDL concentration, one would expect 100 to result in negative blank-corrected signals. The MDL is found by analyzing at least seven aliquots of the matrix of interest containing the analyte at a concentration near the MDL, using the specified equipment and procedure. From the sample observations, S_B is determined and the MDL is calculated from

$$\text{MDL} = t_{n-1, 1-\alpha} S_B \quad (6.6)$$

where S_B is now the standard deviation of the sample measurements, expressed in concentration units and $t_{n-1, 1-\alpha} = .99$ is the student t value corresponding to $n-1$ degrees of freedom and an exceedence probability, α , of 0.01.

A drawback to this method is that the noise, as quantified by S_B , increases with increasing concentration. Therefore, one must accurately guess the MDL in order to prepare a sample from which S_B and the MDL can be determined. The EPA method provides suggestions for making the initial estimate and describes an iterative procedure for converging on the MDL.

Of course, the major difference between these two approaches is that the IUPAC method is based on samples containing no analyte, while EPA specifies that analyte must be present in the MDL determination. Both are based on the specification of a complete analytical procedure.

Obviously, the numerical values obtained by these two methods can differ considerably, and both methods result in complications when one tries to interpret recorded nondetects. For example, it is difficult to make probability statements regarding what analytical results are expected when the actual analyte concentration is between zero and the MDL (which would be the usual case for those values recorded as nondetects). In the IUPAC method, S_B applies only for blanks, and in the EPA method, S_B applies only at analyte concentrations equal to the MDL.

Many problems arise in the analysis and use of nondetect data for water quality management objectives. Perhaps the most significant

problem is that useful information is produced in laboratory analysis, i.e. analytical signals are obtained, which are not reported if the signal is below the MDL (Porter, 1986; Gilliom et al., 1984). An interesting corollary is that users of water quality data tend to associate an unrealistically high level of accuracy with observations which are just above the MDL. Upon reflection, it seems ludicrous to essentially "throw out" one observation and accept another as accurate when the two have almost identical measurement errors.

Several approaches to dealing with the problem of nondetects for water quality management have been suggested. Perhaps the most common, and least satisfactory, is the use of a fixed value in place of the nondetect. McBean and Rovers (1984) examine this approach, discussing the ramifications of using the detection limit, half the detection limit, and zero in data analysis. All of these options were deemed unsatisfactory, and two alternatives were presented. The first was fitting probability distributions to data above the detection limit and then assuming this distribution represents the whole population. The second alternative was the use of nonparametric statistics based on ranks rather than numerical values of observations.

When one must use water quality data which have already been reported as nondetects, one has little choice but to adopt one of these general approaches. The first approach can be used when the management objective is to estimate the characteristics parameters, such as mean and standard deviation, from a censored sample (a record containing nondetects). A comparison and evaluation of methods is presented in Gilliom and Helsel (1984).

Routine analysis of censored monitoring data for the regulatory objective of trend detection is probably better handled with nonparametric methods based on ranks. (See for example Hirsch et al., 1982.) However, one must keep in mind that the problem of small sample sizes for characterizing water quality random variables and for detecting changes will be accentuated when the record is censored.

The prudent approach is to avoid removing information from a data record, if at all possible. One should not, therefore, record observations as nondetects but rather convert all signals to measured concentrations, no matter how small, and include them in the data record. Analytical chemists are understandably reluctant to do this since they do not wish to be accused of implying false accuracy in their results. However, the idea of arbitrarily assigning values to nondetects when actual observations are available would seem to have little merit.

In order to most effectively utilize laboratory measurements of concentrations of water quality variables, especially those at

concentrations near or below the detection limit, one needs information from the laboratory in addition to recorded signals. This information is an estimate of the noise (error) component of the signal at the reported concentration. Laboratories must develop this information routinely in calibration of instruments and quality assurance programs. However, it is rarely reported to the users of laboratory results.

Analytical chemists may be reluctant to adopt this approach since much more work is involved in reporting both measured concentrations and estimates of measurement noise. However, much more information can be obtained from a given number of samples compared to the current practice of reporting only a measurement or a nondetect.

Unfortunately, it is not a straightforward matter to incorporate estimates of measurement error into statistical procedures common to water quality data analysis. Procedures for doing this must be developed from the statistical theory associated with calibration and are fairly complex. Porter (1986) presents a discussion of the relevant theory and provides an example in which the mean and variance of a water quality random variable are estimated while explicitly including knowledge of measurement error.

To summarize this section, one should avoid censoring a sample by reporting nondetects wherever possible. Information on measurement errors should be routinely reported wherever possible. When nondetects are already present in the data record, population characteristics may be estimated from data above to detection limit; and nonparametric methods based on ranks may be used for routine trend analysis. Assigning fixed values to nondetects should be avoided.

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CHAPTER SEVEN

MAJOR CONCLUSIONS AND RECOMMENDATIONS

I. Major Conclusions

- A. Federal requirements for monitoring state or imply four major objectives as follows:
1. determination of background ground water quality
 2. determination of permit compliance
 3. detection of ground water contamination
 4. characterization of the effectiveness of corrective action
- B. State regulatory ground water quality monitoring programs possess several important characteristics as follows:
1. The goals of state laws and regulations dealing with ground water quality parallel those of the federal level. More specifically, the primary objective of state regulatory monitoring is the detection of degradation of ground water quality due to regulated (permitted) facilities.
 2. Due to the impact of RCRA, many states are beginning to statistically analyze ground water quality data. Well defined data analysis procedures which match the objectives of monitoring are not yet in place, however.
 3. Generally, records of ground water quality which are available to state agencies are too short and too irregular for accurate characterization of background water quality.
- C. The most important general statistical characteristics of ground water quality random variables are the following:
1. Ground water quality variables may sometimes exhibit seasonality or predictable cyclic behavior. Seasonality is often reported in the literature but was found by the authors of this report in only 15 out of 193 case study data records.
 2. Ground water quality variables are frequently non-normally distributed. The authors found that less

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than half of the 172 cases studied passed a skewness test for normality at the 95% confidence level. This finding was supported by previous research. Factors which contribute to non-normality in ground water quality variables are often the presence of "less-thans" or "non-detects" and/or a few very large values. A possible explanation for outliers is sampling error. Case study data records tended to exhibit positive skewness, i.e. to be skewed right.

3. Serial correlation is difficult to evaluate in ground water quality random variables. Few researchers have studied the issue extensively, and current data records are generally too short and too irregular for such studies. The authors examined 118 records of "approximately" quarterly data and found 17 cases of significant (95% confidence level) serial correlation. Eight cases were found where serial correlation was significant, but seasonal variation was not.
4. An extensive review of the literature revealed that significant sources of variability or error in ground water quality are the following:
 - a. vertical concentration gradients
 - b. horizontal concentration gradients
 - c. time or volume of pumping
 - d. sample collection procedures
 - e. data management procedures
5. The literature reveals that intervariable correlations are often significant in ground water quality data. No analyses of case study data were performed by the authors of this report to evaluate intervariable correlations, however. To state an apparently obvious fact, the design of regulatory monitoring programs based on intervariable correlations or indicator variables assumes that the leak one is trying to detect will cause a change in the variables being monitored. Selection of indicator variable should be based on the nature of the leak anticipated; not on background intervariable relationships.

II. Recommendations

- A. The following statistical procedures would be well suited to the purpose of characterizing ground water quality variables.
 1. To test for significant differences in means between two seasons, the Student t-test may be used for normally

distributed variables, and the Mann-Whitney test may be used for non-normal variables.

2. To test for differences when more than two seasons are relevant, analysis of variance or the nonparametric Kruskal-Wallis test may be used.
3. The skewness test is preferred for evaluating the normality assumption in ground water quality data.
4. Evaluation of serial correlation is almost impossible for ground water quality records of "typical" length. The recommended procedure is to place 95% confidence limits on sample estimates of the lag-one autocorrelation coefficient. For practical applications, one might be forced to assume that quarterly ground water quality data are usually uncorrelated if they are not seasonal. (The consequences of a bad assumption would be serious, however.)

B. The following recommendations apply to analysis of data for the regulatory objective of detecting changes in ground water quality.

1. A "paired-well" approach to the analysis of ground water quality data from regulated facilities is recommended to account for seasonality and other factors which impact both upgradient and downgradient wells.
2. A tolerance interval approach is suggested as a means of detecting sudden shifts in ground water quality, such as leaks from regulated sites.

C. More general recommendations include the following:

1. Sampling more frequently than quarterly (perhaps monthly), may help to overcome the limitations of small sample sizes. Serial correlation may become more significant as sampling frequency increases, however.
2. To maximize the information content of laboratory data, the recording of observations as "nondetects" should be avoided in favor of recording actual signals (converted to concentrations) from laboratory instruments. Information on the magnitude of laboratory error should also be reported, especially in the region of small concentrations and "noisy" observations.

APPENDIX

Results of Analyses of Case Study Data

Site locations described in Chapter Three

Statistical methods described in Chapters Four and Five

Concentrations in mg/l

Table A.1 California, Acme Landfill

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	2	Qtly	March 78	Dec 84	23	10640	5428
	4				20	11963	7552
	6				22	336	134
Spec. Cond.	2				23	34096	14952
	4				21	37876	19951
	6				20	1875	637
Total Dissolved Solids	2				23	20409	14295
	4				21	23141	13166
	6				22	1016	281
Total Organic Carbon	2				18	80	55
	4				16	95	108
	6				17	15	13
Total Kjeld. Nit.	2				23	79.3	58.1
	4				21	124.3	186.5
	6				22	1.9	1.8
pH	2				23	6.8	0.3
	4				21	6.5	0.3
	6				22	7.2	0.3

Table A.1 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
1200	18000	11000	N	N	N	.005	Y	N
160	24000	7900	Y	N	N	.10	Y	Y
100	580	295	N	Y	Y	.50	Y	N
4100	52000	40000	N	N	Y	.75	N	N
1400	67000	30000	Y	N	N	.10	Y	Y
1100	3200	1800	N	N	Y	.90	Y	Y
2500	74000	20000	Y	N	Y	.50	N	N
620	45000	16000	Y	N	N	.005	Y	N
450	1600	975	N	N	Y	.10	Y	N
23	230	71	N	N	Y	.25	N	N
7	330	37	Y	N	N	--	N	Y
2	44	9	N	N	Y	.50	N	N
8.2	170.0	41.0	Y	N	N	.005	Y	N
0.43	600	7	Y	Y	N	.001	N	N
0.1	6.5	1.3	Y	N	N	.01	N	N
6.1	7.2	6.7	Y	N	N	.10	Y	Y
5.9	7.3	6.1	N	N	Y	.90	Y	N
6.4	7.8	7.2	Y	Y	Y	.50	N	N

Table A.2 California, Baker-Vine Landfill

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	4	approx. semi-annual	June 78	Oct 84	14	4566	1990
	14				19055	9049	
	1				17764	8386	
Total Dissolved Solids	4				14	10339	3254
	14				14	42519	16706
	1				10	38400	20660
Total Organic Carbon	4				12	58	72
	14				12	97	91
	1				8	143	134
pH	4				14	7.0	0.3
	14				14	6.7	0.4
	1				10	6.8	0.5

Table A.2 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
1400	10139	4017	N	N	Y	1.50	N	N
2120	30000	19950	Y	N	Y	-.53	Y	N
10416	32000	13375	Y	N	N	.92	N	N
7800	20000	9150	N	N	N	2.00	N	N
6840	74500	44200	Y	N	Y	-.46	Y	N
20658	74500	24373	Y	N	N	.61	Y	N
10	275	40	N	N	N	2.48	N	N
8	325	71	N	N	N	1.59	N	N
15	450	118	N	N	Y	1.61	N	N
6.7	7.7	7.0	Y	N	Y	.65	Y	N
6.1	7.7	6.7	Y	N	Y	.89	N	N
6.0	7.5	6.9	Y	N	Y	-.33	Y	N

Table A.3 Colorado, Rocky Mountain Arsenal

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	6-2	qtly	Dec 75	May 84	29	45.5	16.7
	8-2		Nov 75	Apr 84	28	29.5	13.0
	33-1		June 75	June 84	32	47.1	23.4
Fluoride	6-2		Dec 75	May 84	30	1.43	0.22
	8-2		Nov 75	April 84	31	1.32	0.37
	33-1		June 75	June 84	32	0.67	0.15
Hardness	6-2		Dec 75	May 84	28	215.5	81.9
	8-2		Nov 75	April 84	31	192.1	72.8
	33-1		June 75	June 84	30	280.3	106.8
Sodium	6-2		Dec 75	May 84	25	91.1	20.3
	8-2		Nov 75	April 84	29	50.7	10.0
	33-1		June 75	June 84	29	63.1	20.8
Nitrate	6-2		Dec 75	May 84	29	4.38	4.79
	8-2		Nov 75	April 84	31	9.71	6.69
	33-1		June 75	June 84	32	11.5	18.70
pH	6-2		Dec 75	May 84	27	7.68	0.323
	8-2		Nov 75	April 84	31	7.06	0.284
	33-1		June 75	June 84	32	7.49	0.251
Sulfate	6-2		Dec 75	May 84	29	112.7	82.8
	8-2		Nov 75	April 84	31	47.2	17.4
	33-1		June 75	June 84	31	198.7	227.8

Table A.3 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
14	92.5	40	Y	N	Y	0.166	Y	N
19	79	25.95	Y	Y	Y	1.092	N	N
26	132.7	39.5	N	Y	N	2.180	N	N
1	1.9	1.41	Y	N	Y	1.009	N	N
0.83	2.9	1.33	Y	N	N	3.173	N	N
0.13	0.89	0.59	N	N	Y	-1.167	N	N
100	430	186.5	Y	N	Y	0.598	Y	N
76	376	196	Y	N	Y	0.121	Y	N
99	500	251.5	Y	N	Y	0.742	N	N
60.2	140	85	Y	N	Y	0.824	N	N
32.1	81.6	48.2	Y	N	Y	1.871	N	N
35.8	157	61	N	N	N	4.387	N	N
0.21	14	1.17	N	N	Y	0.525	Y	N
4	31	7	Y	N	Y	0.757	N	N
0.27	80	5.25	Y	N	N	1.462	N	N
7.12	8.39	7.68	Y	N	Y	0.901	N	N
6.94	8.11	7.69	Y	N	Y	-0.437	Y	N
6.61	7.83	7.53	N	N	Y	-1.155	N	N
10	355	76.9	Y	N	Y	0.797	N	N
9	73	50.4	N	N	N	-1.109	N	N
60.1	1150	127	N	N	N	3.137	N	N

Table A.4 Illinois, Belvidere Municipal Landfill #2

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	G102	Irreg. Qtly	May 74	Jan 83	48	43	30
Total Dissolved Solids	G102				47	729	1206
Iron	G102				39	1.6	3.6

Table A.4 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
12	180	37	Y	N	N	2.78	N	--
4	6900	392	N	N	N	3.69	N	--
0	18.0	0.3	Y	N	N	3.45	N	--

Table A.5 Illinois, Kankakee County

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	G125	approx. qtly	10/18/74	5/3/84	40	8	6
	G135				40	17	13
	G145				42	13	6
Total Dissolved Solids	G125				41	502	232
	G135				41	504	361
	G145				42	1049	508
Temperature (°F)	G125		6/20/77	5/3/84	28	54	11
	G145				29	53	9

Table A.5 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
0	33	7	Y	N	Y	1.96	N	N
1	70	15	Y	N	N	2.29	N	N
0	27	11	Y	N	N	0.55	Y	N
37	1380	463	N	N	N	1.23	N	N
180	2022	402	N	N	N	2.90	N	Y
225	2053	985	Y	N	Y	0.41	Y	Y
39	77	53	N	Y	Y	0.26	Y	N
40	81	53	N	Y	N	0.72	N	N

Table A.6 Illinois, Milan County Landfill

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	G127	approx qly	Sept 76	May 84	37	10	3
	G129		Sept 76		35	21	14
	G111		March 78	30	367	155	
	G125		34	881	712		
Total Dissolved Solids	G127				36	579	115
	G129				35	648	166
	G111				30	2413	874
	G125				32	2944	2002
Total Ammonia	G127				36	1.21	1.11
	G129				33	1.05	0.85
	G111				28	3.94	11.58
	G125				33	30.92	26.19
Total Iron	G127				36	7.38	16.80
	G129				33	2.6	5.10
	G111				29	1.6	3.70
	G125				32	17.0	25.0
Boron	G127				34	0.40	0.9
	G129				33	0.50	1.1
	G111				29	6.7	3.8
	G125				33	2.9	4.2

Table A.6 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
6	24	10	Y	N	Y	2.04	N	N
1	78	18	N	N	N	2.61	N	N
16	610	368	N	N	Y	-0.20	Y	Y
10	1900	868	Y	N	N	-0.03	Y	N
338	1021	556	N	N	N	1.50	N	N
450	1200	608	N	N	N	1.89	N	Y
867	3500	2657	Y	N	Y	-0.39	Y	Y
200	5900	3164	Y	N	N	-0.09	Y	Y
0.05	5.66	1.15	Y	N	N	1.92	N	N
0.05	3.00	0.98	N	N	Y	0.71	N	N
0.05	57.6	1.06	Y	N	N	4.00	N	N
0.05	75.6	32.89	Y	N	N	1.55	N	Y
0.10	76.3	0.60	N	N	N	2.97	N	N
0.10	20.7	0.40	N	N	N	2.68	N	N
0.10	18.0	0.20	N	N	N	3.41	N	N
0.10	90.0	2.90	Y	N	N	1.76	N	N
0.10	4.6	0.10	N	N	N	3.41	N	N
0.00	5.9	0.10	N	N	N	3.94	N	N
0.20	14.8	6.4	Y	N	Y	0.34	Y	N
0.10	23.1	2.0	Y	N	N	3.73	N	N

Table A.7 Illinois, Ogle County

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Total Dissolved Solids	G101 G103	Irreg. Qtly	July 1976	Dec 1982	24 29	414 486	57 98
Total Ammonia	G101 G103				25 29	0.40 0.38	0.44 0.48
Total Iron	G101 G103				21 29	0.2 0.5	0.2 1.2
Temperature (°F)	G101 G103				25 25	52 52	9 8

Table A.7 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
252	532	425	N	N	Y	-.67	Y	N
335	724	469	Y	N	Y	.52	Y	N
0	1.74	0.26	N	N	N	1.39	N	N
0	1.69	0.16	N	N	N	1.47	N	N
0	0.9	0.1	Y	N	Y	1.77	N	N
0	5.3	0.1	Y	N	N	2.98	N	N
37	70	54	N	Y	Y	<0.01	Y	N
37	64	52	N	Y	Y	-.15	Y	N

Table A.8 New York, Babylon Landfill

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	1A	Irreg. Monthly	Oct 1975	May 1977	18	234	102
	2A				18	104	51
	6A				18	66	48
	8A				18	35	27
Spec. Cond.	1A				18	1386	524
	2A				18	583	111
	6A				18	345	130
	8A				18	293	72
Nitrate Nitrogen	1A				18	0.04	0.04
	2A				18	1.40	1.03
	6A				16	1.24	0.30
	8A				18	1.72	1.27
Total Organic Carbon	1A				15	25	27
	2A				15	4	3
	6A				14	3	2
	8A				15	7	4
pH	1A				9	7.2	0.46
	2A				9	7.2	0.42
	6A				9	6.5	0.13
	8A				9	6.3	0.39
Iron	1A				18	24.0	9.97
	2A				18	0.16	0.06
	6A				18	0.23	0.12
	8A				18	0.60	0.45
Sulfate	1A				18	29.7	19.4
	2A				18	43.8	7.9
	6A				18	21.9	3.6
	8A				18	40.1	14.5

Table A.8 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
65	415	242	Y	N	Y	-.04	Y	Not Measured
42	265	92	Y	Y	Y	1.64	N	
34	213	49	Y	N	N	2.05	N	
2.5	103	24	N	N	Y	1.62	N	
695	2090	1450	Y	N	Y	-.07	Y	--
382	800	615	Y	N	Y	-.36	Y	--
227	708	299	Y	N	Y	1.69	N	--
222	450	273	Y	N	Y	.93	N	--
0.01	0.15	0.02	Y	N	N	2.16	N	--
0.02	3.20	1.50	Y	N	Y	.19	Y	--
0.50	1.70	1.30	Y	N	Y	-.69	Y	--
0.34	4.7	1.50	Y	N	Y	.87	N	--
0	111	20	N	N	N	2.19	N	--
0	10	3	N	N	Y	.70	Y	--
0	7	3	Y	N	Y	.79	Y	--
0	13	7	N	N	Y	-.25	Y	--
6.8	8.3	7.2	N	N	Y	1.56	N	--
6.8	8.2	7.0	N	N	N	1.62	N	--
6.25	6.7	6.5	Y	N	Y	-.26	Y	--
6.0	7.2	6.2	N	N	N	1.81	N	--
2.52	43.8	24.8	N	Y	Y	-.10	Y	--
0.04	0.28	0.16	Y	N	Y	.03	Y	--
0.09	0.54	0.22	N	N	Y	.82	N	--
0.17	1.60	0.48	N	N	Y	1.02	N	--
2.0	57.5	32.7	N	N	Y	<.01	Y	--
23.2	56.0	44.2	N	N	Y	-.83	N	--
14.0	28.8	22.0	N	N	Y	-.15	Y	--
23.5	66.0	33.7	Y	N	Y	.76	Y	--

Table A.9 New York, Courtland County

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	35	Irreg.	Nov 1979	Jul 1984	27	43	10
	45		Jan 1980		20	26	3.0
	55		Jan 1980		25	42	15
	65		Apr 1980		23	14	2.6
	85		Nov 1979		27	20	2.3
Nitrate	35				30	4.0	0.79
Nitrogen	45				22	2.8	0.48
	55				26	3.6	1.1
	65				26	2.6	0.47
	85				29	2.3	1.1

Table A.9 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
26	60	44	Y	Y	Y	.01	Y	Not Measured
21	31	25	N	Y	Y	.32	Y	
8.5	66	46	N	N	Y	-.76	N	--
5.5	19	14	N	N	N	-.84	N	--
13	25	21	Y	N	Y	-.98	N	--
1.5	5.5	4.1	N	N	Y	-.86	N	--
2.0	3.9	2.7	N	Y	Y	.53	Y	--
0.34	5.1	3.95	Y	N	Y	-1.16	N	--
1.3	3.2	2.8	Y	N	Y	-1.15	N	--
0.11	4.2	2.5	N	N	Y	-.15	Y	--

Table A.10 New York, Nassau County

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	5187	Irreg.	June 55	March 84	35	3.7	0.88
	3603				37	6.1	1.3
	650				37	10.4	3.7
	3457				50	14.4	7.8
Spec. Cond.	5187				19	33	16
	3603				27	66	10
	650				27	163	42
	3457				34	159	75
Total Dissolved Solids	5187				34	28	12
	3603				33	57	12
	650				32	117	37.5
	3457				46	97	51
Nitrogen as NO3	5187				35	0.03	0.097
	3603				37	2.51	0.656
	650				45	7.10	3.55
	3457				62	5.43	3.71

Table A.10 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
1.2	5.6	3.8	N	N	Y	-0.51	Y	--
3.	9.2	6.2	N	N	Y	-0.30	Y	--
5.6	22	10	Y	N	Y	1.27	N	--
4.0	31.1	13.4	Y	N	N	0.51	Y	--
20	95	30	N	N	N	3.47	N	--
55	90	60	N	N	N	0.98	N	--
110	240	163	Y	N	Y	0.43	Y	--
70	350	142	Y	N	Y	1.08	N	--
13	61	23	N	N	Y	1.23	N	--
39	93	56	N	N	Y	0.99	N	--
40	204	120	Y	N	Y	-0.01	Y	--
20	219	89	Y	N	Y	0.73	N	--
0.	0.53	0.01	N	N	N	4.35	N	--
0.83	3.3	2.6	Y	N	Y	-1.08	N	--
2.25	15.0	6.77	Y	N	Y	0.38	Y	--
0.61	15.0	4.8	Y	N	Y	0.66	N	--

Table A.11 Wyoming, Laramie River Station

Variable	Well Ident.	Sample Freq.	Begin Date	End Date	No. Obs.	Mean	Std. Dev.
Chloride	10b	Qtly	April 77	Oct 85	26	13.5	4.33
	12b				26	23.4	3.61
	2b		27	70.5	21.07		
	6a		Jan 77	27	6.8	1.86	
	6b		April 77	27	58.2	20.90	
	7b		26	49.9	8.10		
	8b		26	16.7	4.72		
	Spec. Cond.		10b				25
12b					25	631.6	41.80
2b					26	2076.2	332.66
6a		Jan 77			24	469.2	14.46
6b		April 77			24	2213.3	337.62
7b					23	1187.3	55.39
8b					23	610.	19.04
Sulfate		10b				26	88.5
	12b				26	134.9	14.92
	2b				27	742.6	194.41
	6a	Jan 77			26	57.6	10.33
	6b	April 77			26	771.1	218.31
	7b				26	283.4	17.33
	8b				25	111.3	12.88
	pH	10b				27	7.87
12b					27	7.79	0.21
2b					27	7.69	0.22
6a		Jan 77			27	7.91	0.21
6b		April 77			27	6.68	0.21
7b					25	7.91	0.19
8b					26	7.83	0.22

Table A.11 (Cont.)

Min	Max	Median	Linear Trend	Seasonal	Normal Chi-Sq	Skew Coeff	Normal Skew	Serial Corr
7	25	12.5	N	N	Y	0.596	Y	N
17	33	23.5	N	N	Y	1.121	N	N
38	127	68	N	N	Y	0.459	Y	N
3	11	6	Y	N	Y	0.342	Y	N
33	113	52	Y	N	N	1.387	N	N
33	64	50	Y	N	Y	-0.051	Y	N
11	31	15	N	N	Y	0.732	N	N
413	670	487	N	N	Y	0.900	N	N
540	710	630	N	N	Y	-0.019	Y	N
1623	2755	2002	N	N	Y	0.683	Y	N
433	491	470	N	N	Y	-0.506	Y	N
1600	2810	2175	Y	N	Y	0.169	Y	N
1070	1270	1190	N	N	Y	-0.408	Y	N
580	655	610	Y	N	Y	-0.356	Y	N
57.5	136	84.7	N	N	N	0.785	N	N
102.5	180	132.8	N	N	Y	0.004	Y	N
410	1183.3	750	N	N	Y	0.439	Y	N
28	71	62.7	Y	N	N	-1.401	N	N
490	1300	698.5	Y	N	Y	0.937	N	N
255	315	281.5	Y	N	Y	0.107	Y	N
87	151	108.7	N	N	Y	1.491	N	N
7.6	8.2	7.85	Y	N	Y	0.406	Y	N
7.43	8.15	7.8	N	N	Y	0.051	Y	N
7.3	8.1	7.67	N	N	Y	0.082	Y	N
7.4	8.3	7.91	Y	N	Y	0.157	Y	N
7.3	8.1	7.67	N	N	Y	0.683	Y	N
7.6	8.3	7.9	N	N	Y	0.461	Y	N
7.3	8.2	7.8	Y	N	Y	0.337	Y	N