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Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load (“The Griffiths Report”)



**Statistical Analysis of
Abandoned Mine Drainage in the
Assessment of Pollution Load**

(“The Griffiths Report”)

Prepared for:

**U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division**

Prepared by:

**John C. Griffiths
Roger J. Hornberger, Pennsylvania DEP
Ken Miller, DynCorp I & ET
Michael W. Smith, Pennsylvania DEP**

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DEDICATION

John C. Griffiths was one of the early leaders in the use of statistics in the geological sciences. As an attest to his world class stature, he was the first recipient of the William C. Krumbein Award by the International Association of Mathematical Geology in 1977, named after one of his contemporaries. Griffiths, Krumbein, Felix Chayes and a few others introduced geologists and geological students to statistical methods in sampling, experimental design, petrology, mineralogy, sedimentology, stratigraphy and other aspects of the geosciences throughout the 1950's, 1960's and 1970's as documented in approximately 100 scientific papers and several text books.

John Griffiths was born on February 29, 1912 in Wales. He earned 3 degrees from the University of Wales including a PhD in 1937 in glacial geology and petrography, a Diploma of Imperial College at the Royal College of Science in London, and a second PhD from the University of London in 1940. He was employed as a research petrographer on oil well drilling projects from 1940 to 1947 in Trinidad, where he was married on July 26, 1941. He was a professor in geosciences at the Pennsylvania State University from 1947 to his retirement in 1977, and thereafter was a Professor Emeritus until his death on June 2, 1992 in State College, PA. The day before his death at age 80, he was conducting research in the Earth and Mineral Sciences Library at Penn State. During his many years as a professor, he served as the Head of the Department of Mineralogy (and Geochemistry) from 1955 to 1966, and as the Director of Planning Research for the entire University from 1969 to 1971.

Dr. Griffiths was an excellent teacher who instilled scientific rigor and an appreciation for proper sampling and the use of statistics in the minds of many students. While at Pennsylvania State University, he taught univariate statistics, bivariate statistics, and multivariate statistics; periodically, he also taught a course in time series analysis. New graduate students, relying upon the foundation of their undergraduate studies, would be confronted by this feisty Welshman, armed with more than 20 years of data on a local stratified gravel deposit from previous classes, saying things like "You call yourselves geologists; you can't even tell me how many layers there are in this gravel deposit." Students soon learned that Dr. Griffiths was challenging them to use statistical analysis as a guide to the unknown in a scientific method for solving problems in the geosciences.

J.C. Griffiths approached teaching, research and much of life in general, with a blend of humor, history, and lessons learned from other sciences, observations from current events, and a strong foundation of scientific rigor and ethics. With the advances in computer science in the 1950's and 1960's, Griffiths expanded his areas of interest into related fields of computer modeling, operations research and cybernetics. In the 1960's and 1970's, he proposed drilling the entire United States on a 20-mile grid spacing, wherein approximately 7500 drill holes each 10,000 to 15,000 feet deep would almost certainly result in the discovery of billions of dollars worth of oil, gold, uranium, zinc, copper and other valuable minerals overlooked by conventional "hit-and-miss" type of exploration. In the early days of research on the correlation between cigarette smoking and the incidence of lung cancer, Griffiths was requested to meet with a famous statistical researcher for dinner the evening before his cancer research speech at the University. Griffiths was a smoker at that time, and his recollection of the evening was, "I

took one look at that man's statistics and I knew that I had 2 choices: I either had to give up cigarettes or give up statistics.”

Following his retirement from the full time faculty in 1977, J. C. Griffiths worked with the U. S. Geological Survey in Reston VA and continued his research with graduate students on quantifying the geology of the world by country for mineral resource assessment purposes. He served as a consultant to DER (now DEP) and EPA from 1984 to 1988 on a cooperative project to support development of Pennsylvania's Coal Remining regulatory package.

Beyond his many professional accomplishments, John C. Griffiths was a great person. This document was prepared in his honor and with great respect for his accomplishments as a geostatistician, a teacher, and a major contributor to our understanding of sedimentary and geochemical processes.

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Chapter 1: Introduction

From 1984 through 1988, the U.S. Environmental Protection Agency (EPA) and the Pennsylvania Department of Environmental Resources (PA DER, now PA DEP) studied the water quality of long-term pre-existing discharges from abandoned mine lands throughout Pennsylvania as part of a cooperative project on remining. Water quality data from these discharges were examined using univariate, bivariate, and time series statistical analyses to assess coal mine drainage discharge behavior. The results of the statistical analyses were included in a series of eight unpublished reports prepared for PA DEP and EPA by Dr. J. C. Griffiths of the Pennsylvania State University in 1987 and 1988.

This report presents a compilation of the work by Dr. Griffiths and co-authors and was prepared by PA DEP and EPA, to support proposal of the Coal Remining Subcategory under existing Coal Mining industry regulations (40 CFR part 434). This report specifically supports statistical procedures provided in EPA's *Coal Remining Statistical Support Document* (EPA-B-001-001), and is intended to be a companion to that document. Chapter 1 of the *Coal Remining Statistical Support Document* contains a description of the remining program history in Pennsylvania from 1984 to 1999, including the development of the REMINE computer program and permitting procedures used in issuing approximately 300 remining permits during that time period. Chapter 1 of the Statistical Support Document also contains the results of an evaluation of state remining programs in 20 states that was completed by the Interstate Mining Compact Commission (IMCC).

Several publications described and documented the mining engineering and treatment costing components of the original cooperative remining project of EPA and PA DER (listed and briefly described in Chapter 1 of the *Coal Remining Statistical Support Document*), but the statistical work of Dr. J.C. Griffiths and co-authors was not published or widely disseminated, and John C. Griffiths died at age 82 in June, 1992. This report was compiled, edited and completed by his co-authors and DynCorp, I & ET. J.C. Griffiths is listed as the major author posthumously because this document contains his original work and is a tribute to him and his work.

There are several additional correlations between this report and the *Coal Remining Statistical Support Document*.

- Chapter 2 of the *Coal Remining Statistical Support Document* contains descriptions of the three fundamental acid mine drainage discharge types and their respective behaviors (flow and water quality relationships) that are based on work done in the statistical studies of the Arnot, Ernest, and Markson discharges featured in Chapters 4, 6, and 8 of this report.
- Chapter 5 of the *Coal Remining Statistical Support Document* includes numerous figures and tables depicting various options in baseline pollution load development (e.g., Table 5.1a) that are based upon the data sets in Chapters 4 through 8 and Appendices A through F of this report.
- Chapter 5 of the *Coal Remining Statistical Support Document* contains additional data from 1988 to 1999 of the Fisher and Markson sites, providing excellent additional information on the long term variations in these discharges.

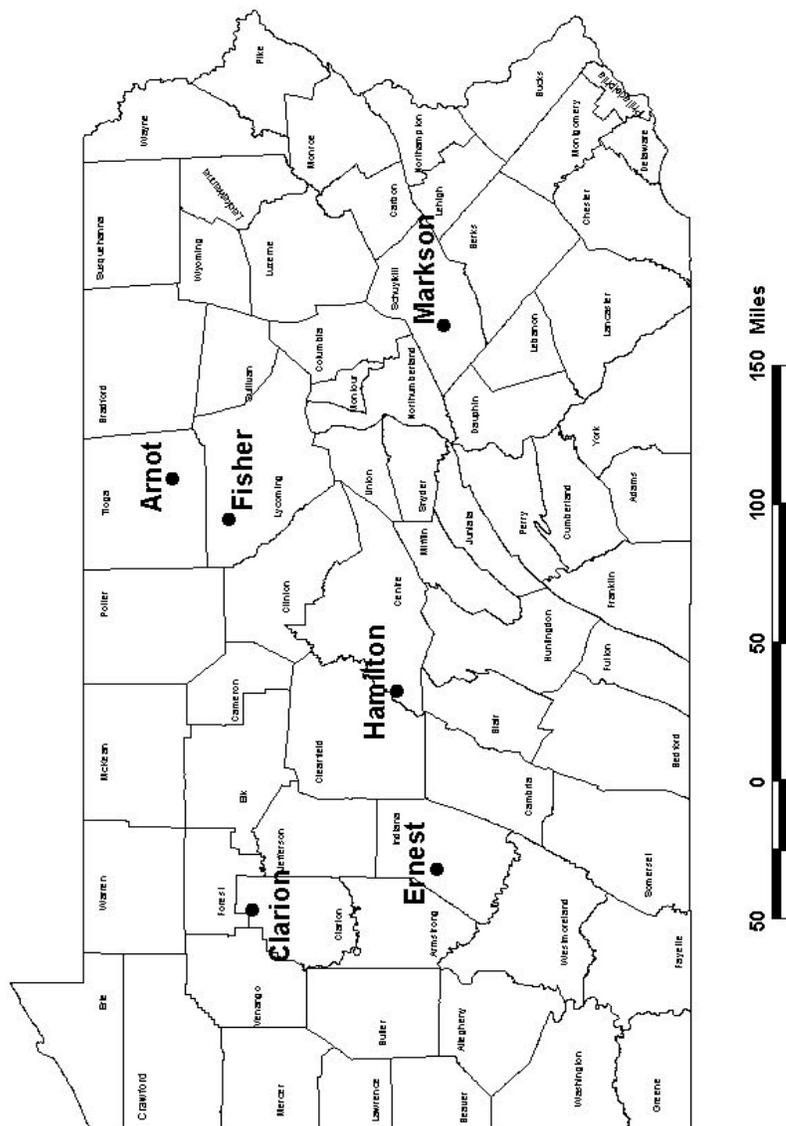
The establishment of the baseline pollution load for a coal remining permit requires the proper sampling and chemical analysis of the abandoned mine drainage discharges, and the appropriate statistical analysis of the flow, water quality and pollution load data. The term proper sampling in this report, is taken in two contexts: (1) following the recommended procedures for collection of surface- and ground-water samples, (including measurements of flow and water quality parameters, and fixing, storing and transporting the samples to the laboratory for chemical analyses), and (2) collecting a sufficient number of samples over an adequate duration and sampling interval in order to be representative of the variations in flow and water quality of the discharges throughout the year.

Guidelines and protocols for water sample collection from EPA, the U.S. Geological Survey (USGS), and other sources, are compiled in Table 9.1. These 14 manuals and related publications represent some of the most recent technical guidance disseminated by Federal agencies on water sampling. Much of this information is founded on common sense and earlier publications on this subject, and include for example, recommendations, sampling streams and major mine discharges at approximately mid-stream and mid-depth to avoid unrepresentative effects of surface debris, bottom sediments, chemical stratification or lack of mixing near stream banks. Water sampling procedures are as important as the laboratory analysis and the statistical analysis of the discharge data. If the water sampling procedures are flawed or unrepresentative, the laboratory analyses, regardless of its high degree of accuracy and precision, may be meaningless. Similarly, the most rigorous statistical analysis may be worthless if it is based upon faulty laboratory analyses or flawed sampling procedures.

The statistical aspects of proper sampling are summarized in Chapter 9 of this report and are discussed in numerous other references including Griffiths (1967) and Griffiths and Ondrick (1968) concerning the proper sampling of geologic populations. In statistical analyses, it is always important to work with samples that are representative of the population from which they are drawn (see Chapter 2 of this report). Since most of the abandoned mine discharges included in this report flow continuously, there is an almost infinite number of samples that could be drawn throughout the water year. For example, one sample collected every hour equals 720 samples per month or 8,760 samples per year. Representative sample collection should be assessed in regards to practicality, feasibility, and cost.

Chapter 2 of this report provides an introduction to the statistical methods that may be employed in establishing baseline pollution load, and Chapter 3 describes the data analysis algorithm that was developed for evaluating mine drainage discharges (see Figure 1.2a of the *Coal Remining Statistical Support Document* and Figure 3.1 of this report). Abandoned mine drainage discharge data from six sites in Pennsylvania are statistically analyzed and presented in graphs and tables in Chapters 4 through 8 and Appendixes A through F of this report. The locations of these sites are shown in Figure 1.1. More detailed site maps and descriptions of the site characteristics are included in the beginning of each chapter. Chapter 9 is a summary of the statistical analyses presented throughout this report, with emphasis on the interpretations of time series analysis and quality control limits.

Figure 1.1: Map of Pennsylvania Counties and Mine Sites



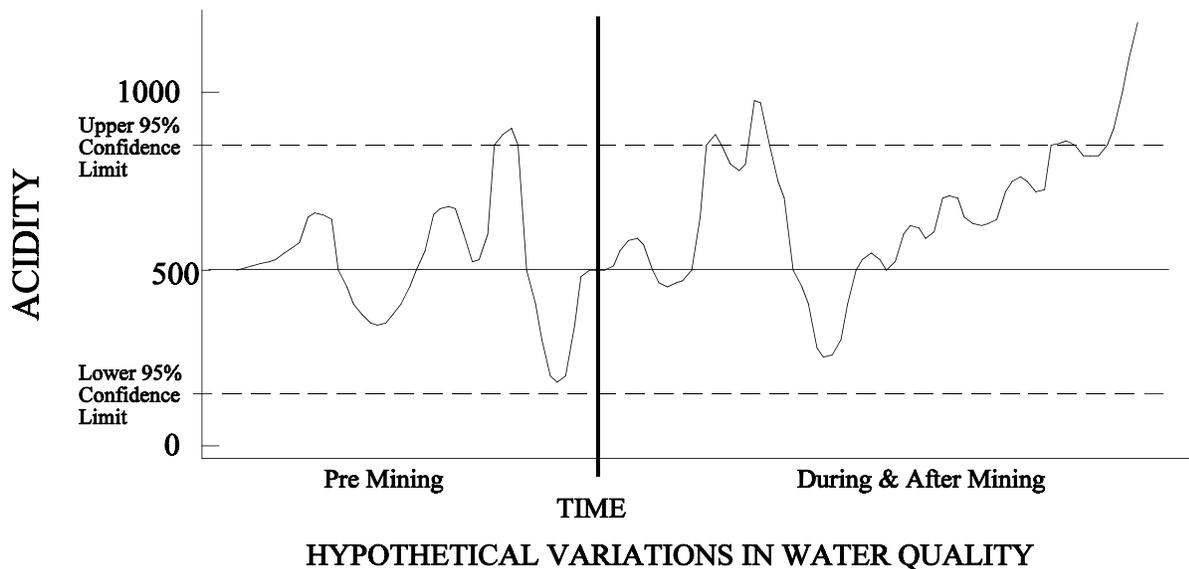
Chapter 2: Statistical Analysis of Mine Drainage Data

If discharges from abandoned mines did not vary in flow or water quality parameters through time, it would not be necessary to use statistics to determine the baseline pollution loads of a remining site. In fact, the baseline determination would involve little effort, in terms of representative sampling and chemical and data analyses. A mine operator or regulatory agency could simply collect one sample to initially establish the baseline flow and water quality, and then collect a second sample at some later time before remining commences to document that the flow and water quality parameters do not vary through time. However, abandoned mine discharges typically vary significantly in flow and/or quality throughout the water year, and it is necessary to use statistics to quantify and explain these variations. Data representing this variation and the statistical analysis of such variation are presented in the succeeding chapters of this report. This chapter provides an introduction to the statistical methods that may be employed in determining the baseline pollution load.

Variation

The fundamental problem to be addressed in determining baseline pollution load is how to statistically summarize the natural variations in flow and water quality parameters before remining commences, in order to enable the separation of mining-induced changes in pollution load from natural seasonal variations in pollution load during and following remining operations. This problem is depicted in Figure 2.1, which shows hypothetical variations in acid load of an abandoned mine discharge before (pre), during, and after remining. It is important to note that Figure 2.1 is presented for graphical description of statistical triggers only and that the after-mining scenario represented in this figure is atypical. In almost all cases, remining will improve water quality. Whatever the case, water quality data should be plotted and statistically analyzed to determine whether adverse effects have occurred.

Figure 2.1: Example of Acid Load Variation Before, During, and After Remining



In Figure 2.1, the acid load varied greatly before remining commenced ranging from nearly zero pounds of acidity per day (lbs/day) to nearly 1,000 lbs/day. Observe that before remining, the discharge usually varies somewhat symmetrically above and below the central value of 500 lbs/day (central tendency) and that the variations are generally contained between the values of 50 lbs/day and 950 lbs/day which have been labeled the lower and upper control levels. Also note that the acid load was higher than the upper control level on one or two occasions before remining commenced. However, during remining the acid load was above the upper control level much more frequently, while the acid load is still varying somewhat symmetrically above and below the central tendency value for at least the first two years during remining. Finally, during the last three years of remining and following the completion of remining, the acid load still varies above and below the central tendency value, but there appears to be a trend of increasing acidity between the central tendency value and the upper control level.

In order to determine baseline pollution load, it is necessary to statistically analyze the data to find a measure of central tendency (e.g., mean or median) and a measure of the patterns of variation or the dispersion of the individual observations (i.e., samples around the central tendency as shown in Figure 2.1). In order to separate mining-induced changes in pollution load from natural seasonal variations, it is necessary to develop a statistical mechanism to determine when variations in the pollution load are out of control; that is, when significant deviations from the pre-remining baseline have occurred which can be attributed to factors other than natural seasonal variations (e.g., problems within remining operations, unrepresentative baseline, inappropriate monitoring).

There are two types of variation in pollution load which are of interest in evaluating monitoring data during and after remining in order to determine whether the variations are out of control from the established baseline conditions.

- Dramatic Trigger - The first and most obvious pattern of variation occurs when there are a series of extreme events which consistently exceed the upper control level as shown in Figure 2.1 during the first two years of remining. During this time, the variation pattern indicates a sudden and dramatic increase in pollution load which may be attributed to remining, and which is referred to as the dramatic trigger.
- Subtle Trigger - The second pattern of variation of concern is a trend of gradually increasing pollution load (as shown in the right side of Figure 2.1,) where the general pattern of acid load observations is increasing above the baseline central tendency value for several years without ever exceeding the upper control level. In this case, when the central tendency values are calculated for each water year during remining, a corresponding gradual increase in central tendency values will be detected until a significant difference exists between the baseline central tendency and a central tendency calculated for a water year after remining has commenced. As this second pattern of variation is much less dramatic than the first, and takes much more time and effort to detect, it is referred to as the subtle trigger.

The reason that these two patterns of variation are referred to as triggers is that they can be used to set off or initiate the requirement for a mine operator to treat a pre-existing discharge to a

numerical effluent limitation. In issuing a remining permit, the regulatory authority makes a determination that the site can be mined without causing additional pollution, and that the pollution abatement plan in the permit application demonstrates that the existing baseline pollution load will be reduced. The mine operator and the regulatory authority anticipate environmental improvement through remining without the need to treat the pre-existing discharge. However, the possibility exists that degradation of the discharge may occur, temporarily or permanently, as the result of remining if the pollution abatement plan is not implemented as required or if unforeseen circumstances develop.

If fair and reasonable consideration is given to the concerns of the mine operator and protection of the environment, the treatment triggers must be carefully established so that they are: (a) not set off prematurely or erroneously, adversely affecting the mine operator, or (b) set off too late resulting in additional mine drainage pollution without treatment. Even the most thorough representative sampling program of a given water year may not capture the most extreme events, because the worst storm (flood) and the most severe drought are rare events and do not occur in every water year. Although it is unreasonable to require a mine operator to collect baseline water samples until the 100 year storm event or a significant drought are captured, it is also unreasonable to require the mine operator to commence treatment the first time that the extreme event or upper control level of the baseline is exceeded. The reagent costs alone for treating some pre-existing pollutional discharges can be several hundred dollars per day and the total cost of building a treatment plant can be more than one million dollars. Costs for treatment of some worst case post mining discharges in the State of Pennsylvania were as high as \$ 700 /day (hydrated lime). Cost for construction of these discharges were greater than \$ 2.1 million.

Conversely, the regulatory authority is not fulfilling its environmental protection mandate if the upper control level and extreme events of baseline are routinely being exceeded and the additional mine drainage pollution effects are obvious, but treatment has not yet been required because statistical analysis of the water year has not been completed. In light of these concerns, problems that need to be resolved statistically with respect to the dramatic and subtle triggers are:

- Dramatic trigger - how high should the upper control level or tolerance level be, and how many excursions above this upper level are tolerable before it is determined that the system is out of control and treatment of the discharge must be initiated.
- Subtle trigger - how much deviation from the baseline central tendency value is tolerable in succeeding water years before it can be determined that a significant difference exists.

Both of these problems may be addressed statistically with a relatively simple quality control approach to the data.

Normal Distribution

The quality control approach used in this report and much of statistical work in general, is dependent upon the frequency distribution of the sample data. It is important to collect representative samples, because it is usually impossible or impractical to measure and analyze

the entire population of the parameter being studied. Whether the samples represent variation in a single point through time (e.g., seasonal variations in the acidity of an abandoned mine discharge) or spatial variations in a parameter of interest (e.g., variations in the mean acidity of surface mine discharges from the lower Kittanning coal seam of 200 sites in western Pennsylvania), one of the first steps of statistical analysis, typically, is to plot the frequency distribution of the data. According to Sir Ronald A. Fisher (1970), the founder of many important statistical advances since the 1920's:

“The idea of an infinite **population** distributed in a **frequency distribution** in respect of one or more characters is fundamental to all statistical work. From a limited experience, for example, of individuals of a species, or of the weather of a locality, we may obtain some idea of the infinite hypothetical population from which a sample is drawn, and so of the probable nature of future samples to which our conclusions are to be applied. If a second sample belies this expectation we infer that it is, in the language of statistics, drawn from a different population; that the treatment to which the second sample of organisms had been exposed did in fact make a material difference, or that the climate (or the methods of measuring it) had materially altered. Critical tests of this kind may be called tests of significance, and when such tests are available we may discover whether a second sample is or is not significantly different from the first.” (p. 41)

Fisher (1970) also states:

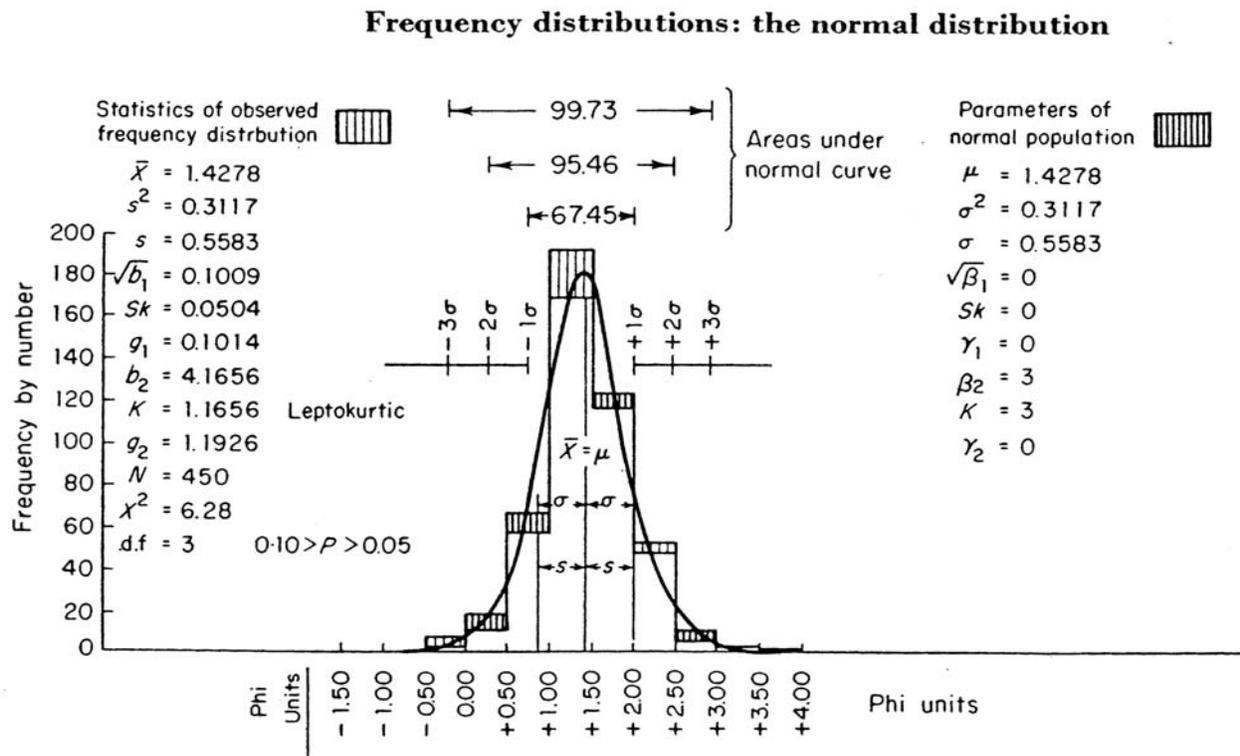
“Statistics may be regarded as (i) the study of **populations**, (ii) the study of **variation**, (iii) the study of methods of the **reduction of data** (p. 1)... [and] ...A **statistic** is a value calculated from an observed sample with a view to characterizing the population from which it is drawn.” (p. 41)

The frequency distribution is a graphical summary of the sample data, and its shape and accompanying summary statistics enable a greater understanding of how a variate behaves. This understanding is gained through comparison of the frequency distribution of observed data to the shape and characteristics of a known mathematical or theoretical distribution, such as the normal distribution or binomial distribution. The normal distribution shown in Figure 2.2 is the most widely known and most useful frequency distribution. It is also known as the Gaussian error curve or bell-shaped curve.

The key statistical parameters of a normal frequency distribution are the mean, as the measure of central tendency (i.e., shown as \bar{X} in Figure 2.2), and the standard deviation or the variance, as the measure of variation or dispersion (i.e., the standard deviation is shown as $\hat{\sigma}$ in Figure 2.2). The mean is the arithmetic average of the data, which is computed by dividing the sum of all of the observations by the total number of observations. The variance is the sum of the squares of the deviations of all of the observations from the mean. The standard deviation is the positive square root of the variance.

According to Fisher (1970) and Griffiths (1967), the sample mean (\bar{X}) and standard deviation ($\hat{\sigma}$) determined from a random sample are best estimators of the corresponding population mean (μ) and standard deviation (σ) in a normal distribution. They are defined as "best estimators" because these statistics are consistent, efficient, and sufficient, and in the most desirable outcome, unbiased as well. A primary goal of parametric statistical analysis is that the statistical estimators (e.g., mean and standard deviation) of the sample distribution will converge on the population parameters (i.e., the true mean and variance of the entire population). Most parametric statistical methods, including tests of significance, are based upon: (a) the use of the mean and the standard deviation as best sufficient statistical estimators, and (b) the assumption that the sample data are normally distributed.

Figure 2.2: Example of Normal Distribution



In addition, probability statements, which are used in significance testing, quality control techniques and other statistical methods, are frequently based upon some special properties of the normal distribution (see Griffiths, 1967, pp. 263 – 267). The area under the curve of the normal distribution in the interval between the mean minus one standard deviation and the mean plus one standard deviation (as shown in Figure 2.2, from Griffiths, 1967, p. 259) is 67.45%, while 95.46% of the area of the normal distribution is contained in the interval of the mean plus and minus two standard deviations (i.e., $\bar{X} \pm 2 \hat{\sigma}$). Therefore, from the table of areas of the

normal distribution it may be stated that 95% of the area of the distribution will be contained in the interval of $\bar{X} \pm 1.96 \hat{\sigma}$, Griffiths, 1967, p. 265).

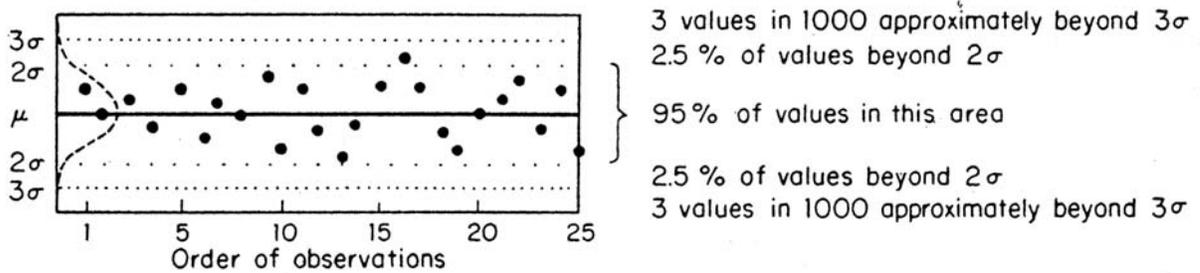
Quality Control - Normal Distribution

The type of statistical analysis known as quality control was largely developed by Shewhart (1931, 1939) and others to evaluate tolerable amounts of variation in manufacturing processes. Since then, the quality control approach has been applied to many other fields of study. Many of the variates studied in very large samples, such as the number of defective light bulbs produced by a manufacturing process, were empirically shown to closely approximate a normal distribution. Consequently, the most typical applications of quality control statistics involve a normal distribution.

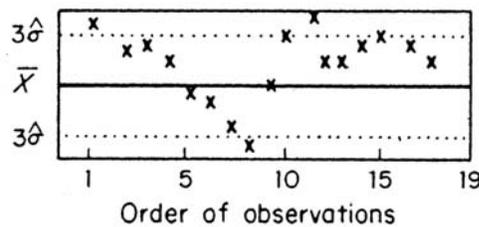
The frequency distribution of the data is essentially arranged along the vertical axis of the quality control graph as shown in Figure 2.3. The actual histogram of value classes is typically omitted from the graph. The mean of the data set, or grand mean of the means of sets of observations, is usually plotted as the measure of central tendency. Quality control levels, known as confidence intervals, are established at plus and minus two or three standard deviations from the mean. Individual observations through time, or comparisons of sets of data representing variations in operator performance, are then plotted along the horizontal axis in order to evaluate the patterns of variation in these observations with respect to the confidence intervals around the mean. As 95.46% of the area of the normal frequency distribution is contained in the interval of the mean \pm two standard deviations, it is expected that approximately 95 out of 100 observations will occur within the confidence intervals.

Figure 2.3: Example of a Quality Control Graph (Griffiths, 1967, p. 318)

According to Griffiths (1967):



(a)



(b)

If the observations are in control, they will fluctuate randomly around the mean value, and some 5 in 100 will fall outside the 2σ limits or 3 in 1,000 will be expected outside the 3σ limits. If a number of observations exceeding these expectations fall outside the control limits, these observations may be looked upon as not belonging to the same population.

The fact that the observations are ordered, however, permits an extension of this generalization; the observations need not fall outside the limits to indicate lack of control. For example, in an industrial process which produces a homogeneous product when the process is in control, the wear on a machine may develop gradually; then a series of observations will show a systematic trend, i.e., the characteristic of random variation will be lost. Such trends arise from a systematic bias, and it is customary to search for an “assignable cause” and remove the interfering source of variation by replacing worn parts in the machine and so on. The systematic trend may appear and the presence of such a trend warns the observer that his observations are not in control (p. 318).

Asymmetric Distribution

A major problem that is frequently encountered in the statistical analysis of water quality parameters and many other variates of natural systems behavior is that the sample data are not normally distributed (Reimann and Filzmoser, 2000). In analyzing the concentrations of acidity, iron, sulfates, or other water quality parameters of abandoned mine discharges, ground water and surface water, it is typical to have many small valued observations in the data set and a few very large values representing extreme events. This type of behavior appears to be relatively common for variates which are related to seasonal variations, climatic effects, and geological or biological systems (for examples, see Aitchison & Brown (1973), Griffiths (1967), and Krumbein & Graybill (1965)). The frequency distribution for this type of variate is highly asymmetric as shown in Figure 2.4. The few very high valued observations cause the frequency distribution to have a long tail toward the high extremes, which is a condition of asymmetry termed positive skewness.

Figure 2.4 : Stem-and-leaf of Discharge (Example of Asymmetric Distribution)

N = 81		
Leaf Unit = 0.10		
40	0	011110000022222222222222223333344444444
(24)	0	5555555555666666777888899
17	1	0123334
10	1	69
8	2	13
6	2	69
4	3	014
1	3	
1	4	
1	4	
1	5	0

In the normal frequency distribution, the values are symmetrically distributed around the mean, and the mean and standard deviation are best statistical estimators of the population. In a highly skewed frequency distribution, the mean may not be the best estimator of central tendency, and the standard deviation may not be the best measure of dispersion.

For example, the few extreme values bias the mean toward the high values, and 95% of the area of the curve is not contained within ± 2 standard deviations from the mean. In cases where the frequency distribution is not normal, the concept of the quality control approach may still be pursued, but data analysis adjustments must be made to either: (a) transform the observed frequency distribution to approximate normality, or (b) employ different statistics (e.g., use of the median instead of the mean) in the quality control technique.

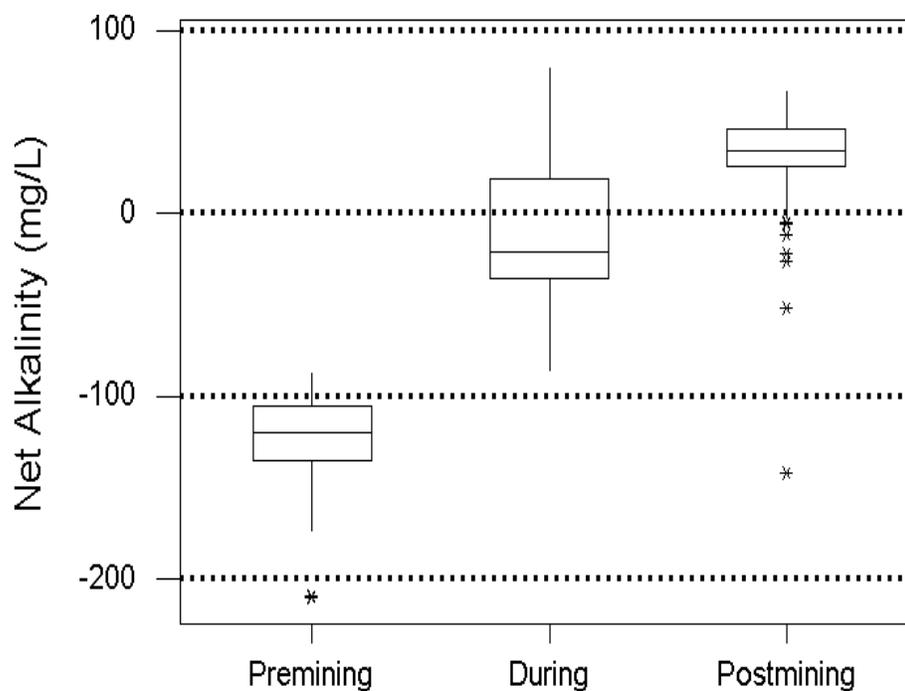
The logarithmic transformation of the data is usually the most effective transformation to reduce positive skewness in the frequency distribution. The lognormal distribution had been extensively described by Aitchison and Brown (1973) and examples of lognormal behavior of variates are found in Griffiths (1967), Krumbein and Graybill (1965) and other sources. However, a logarithmic transformation of the raw data will not solve all problems of asymmetry or other conditions of non-normality of the frequency distribution. Additional information on transformations of data is described later in this chapter and in Box and Cox (1964), Griffiths (1967, p. 306), and Krumbein and Graybill (1965, p. 216).

In order to evaluate different statistics that may be applicable to the quality control approach, it is necessary to explain and differentiate nonparametric statistics, distribution free statistics, and order statistics. It is also necessary to compare exploratory data analysis with confirmatory data analysis.

- Conventional Parametric Statistical Analysis - statistical estimators, such as the mean and standard deviation, are used to approximate the corresponding parameters of the population, the true mean and variance.
- Nonparametric Statistical Analysis - tests of significance are performed without depending on the constraints of a known frequency distribution and the parameters of that known frequency distribution (e.g., the mean and variance of the normal distribution). Nonparametric statistical tests are also used where the scale level of the data are only nominal or ordinal, rather than on interval or ratio scales used in more rigorous statistical analyses. However, if the data conform to a known frequency distribution, there are parameters for that distribution.
- Distribution-free Statistics - is used to describe statistical analyses where parameters are estimated independently of the shape of the frequency distribution, such as the use of the chi-square statistic to test the class by class departure from the expected value.
- Order Statistics - is applied to statistical analyses where the shape of the frequency distribution is important, but is evaluated less rigorously than in conventional parametric statistical analyses. In order statistics, the median is typically used as the measure of central tendency instead of the mean, and quartiles or related values are typically used to measure dispersion, the spread of values about the median, or the shape of the distribution. The position of the median in an ordered set of observations is the middlemost position. For

example, when 15 values are ordered from low to high, the depth (position) of the median is at the $(N+1)/2$ position = 8th position. The position of the two quartiles (Q_1 , Q_3) in this ordered set is halfway between the median and the extremes (e.g., lower quartile (Q_1) is at the $(8+1)/2 =$ midway between the 4th and 5th observation). The quartile (Q_1 in this case), is found by counting in from either extreme to the 4th observation. The quartiles essentially divide the frequency distribution into fourths, so that half of the values in the distribution are contained in the interval between the lower quartile and the upper quartile as shown in Figure 2.5 (i.e., within box). Other values of spread or dispersion are similarly determined based upon their rank or order in the frequency distribution.

Figure 2.5: Net Alkalinity Boxplot for Fisher Mine Site Discharge (from U.S. EPA Coal



Remining Statistical Support Document, March 2000, EPA-821-B-00-001)

As a final note on the relationships of the various frequency distributions discussed herein and elsewhere (see Fisher (1970), Fisher (1973), Griffiths (1967), Krumbein and Graybill (1965) and Tukey (1977)), regardless of the shape of the frequency distributions in samples of water quality parameters or almost any other variable of interest, the distribution of the means of sample sets or means of repeated sampling efforts tend to be normally distributed. Generally, frequency distributions tend toward normality as the number of observations in the sample set becomes very large (i.e., greater than 1 million observations). However, most samples of mine drainage

data used in remining permitting and monitoring will contain a relatively small number of observations (i.e., less than 30).

Exploratory and Confirmatory Data Analyses

Most of the statistical analyses discussed thus far, especially significance tests, can be included in the realm of confirmatory data analysis rather than exploratory data analysis.

According to Tukey (1977):

The principles and procedures of what we call confirmatory data analysis are both widely used and one of the great intellectual products of our century. In their simplest form, these principles and procedures look at a sample -- and at what that sample has told us about the population from which it came -- and assess the precision with which our inference from sample to population is made. We can no longer get along without confirmatory data analysis. **But we need not start with it....**(p. vi)

Once upon a time, statisticians only explored. Then they learned to confirm exactly -- to confirm a few things exactly, each under very specific circumstances. As they emphasized exact confirmation, their techniques inevitably became less flexible. The connection of the most used techniques with past insights was weakened. Anything to which a confirmatory procedure was not explicitly attached was described as "mere descriptive statistics," no matter how much we had learned from it (p. vii).

Exploratory data analysis is detective work... Confirmatory data analysis is judicial or quasi-judicial in character.... Unless the detective finds the clues, judge or jury has nothing to consider. **Unless exploratory data analysis uncovers indications, usually quantitative ones, there is likely to be nothing for confirmatory data analysis to consider.** (p. 1).

From the preceding discussion of statistical analyses, it is apparent that there are many statistical methods and approaches to analyzing data. In order to establish the statistical methods to be used in analyzing abandoned mine discharge data for remining permitting and monitoring, it is necessary to consider the relationship between the characteristics of the sample data and the types of questions to be addressed in determining the baseline pollution load of the discharges. Sometimes, the characteristics of the available data do not lend themselves well to the type of statistical analysis which would be most appropriate to solve the problem. The type of statistical analysis which is: (1) appropriate to apply to a specific data set, and (2) desired or necessary to answer specific questions about the data depends upon numerous factors. These factors include:

- the sampling method,
- the number of observations included in the sample,
- the interval between observations in time (or space),
- the number of measurements performed (e.g., analyzing a water sample for 12 chemical constituents),

- the scale level of the data (i.e., nominal, ordinal, interval, ratio), and
- the frequency distribution of the data.

Univariate/Bivariate and Multivariate Analysis

Statistical analyses which evaluate a single variable are referred to as univariate analyses, while bivariate analyses evaluate the relationship between two variables. Multivariate statistical analyses concurrently evaluate the relationships among more than two variables. Statistical methods involving the frequency distribution of a variable (e.g., chi-square “goodness of fit” test, T-test of the significance of means, F-test of variance ratios) are examples of univariate statistical analyses. Linear regression and correlation (e.g., correlation coefficient (r), and coefficient of determination (r^2)) are examples of bivariate analyses, while multiple regression, factor analysis, principal components analysis, and cluster analysis are examples of multivariate analyses.

It is obvious that it will be very difficult, if not impossible, to use a univariate statistical method to solve a multivariate problem. For example, assume a mine drainage data set contains 100 water samples (i.e., number of observations, $N = 100$) which have been analyzed for 20 chemical constituents (i.e., number of parameters, $p = 20$), an $N \times p$ data matrix of 100×20 results, within which some of the parameters may be highly correlated or dependent upon each other (e.g., acidity, sulfate, and iron may vary in a closely associated pattern). If the problem to be solved is “how many independent sources of information are contained in the data matrix,” a multivariate or “p-dimensional” problem exists that should be addressed with a multivariate statistical method such as principal components analysis or factor analysis. The evaluation of the shape of the frequency distribution of any or all of the 20 variates, in a univariate statistical context, may be an important part of the data analysis process, but it would not solve the multivariate problem.

As the level of sophistication and rigor of the statistical analysis increases from univariate through bivariate and multivariate to include some very powerful statistical methods such as time-series analysis, the requirements placed upon the quality of the data set increase in a corresponding manner. As described earlier, many parametric, univariate statistical methods are based upon the assumption that the sample data are normally distributed. Many bivariate statistical methods, such as linear regression which uses a least-squares method to determine a best fitting regression line, assume that the scatter of data points (when the two variates are plotted together) occurs in a uniform pattern, known as homoscedasticity. In general terms for correlation and regression analyses, this means that: (a) the scatter of the data points does not increase as the data values of the two variates increase, and (b) the data are normally distributed orthogonal to the regression line (i.e., within sections drawn perpendicular to the regression line at equal intervals along the line). Many multivariate statistical methods are based upon the assumption of joint normality of the data matrix (i.e., that all of the variates are normally distributed). Most multivariate statistical analyses are also greatly impeded by missing data (e.g., where 75 of 100 water samples were analyzed for 20 parameters, and the remaining 25 samples were analyzed for 12 parameters), as adjustments are made to the data matrix in order to enable the use of the matrix algebra necessary to mathematically solve the problem. The proper use of time series analysis generally requires a very large number of observations, equally spaced in time (i.e., equal intervals between observations), with no missing data.

Time Series Analysis

As stated earlier, the fundamental statistical problem to be addressed in determining baseline pollution load for remining permitting and monitoring purposes is how to summarize the natural variations in flow and water quality parameters before remining commences, in order to enable the separation of mining-induced changes in pollution load from natural seasonal variations in pollution load during and following remining operations. Conceptually, this is the type of statistical problem which is ideally solved by time-series analysis or a specialized area of time-series analysis, known as intervention analysis. However, the data quality requirements for these types of statistical analyses will exceed the available data for most remining cases, and to require remining permit applicants to collect sufficient data for these analyses would be an onerous and expensive task. The principles of time-series analysis will be briefly introduced here, and more fully explained in later Chapters.

The use of time series analysis in this report is chiefly for research purposes where adequate data exist. The results of research with time series analyses of relatively large mine drainage databases provide a better understanding of the behavior of abandoned mine discharges as they vary through time, and facilitate the application of a relatively simple quality control approach to the statistical analysis of the smaller sets of discharge data typically used in computing baseline pollution load in remining permits.

According to Vandaele (1983):

A time series is a collection of observations generated sequentially through time. The special features of a time series are that the data are ordered with respect to time, and that successive observations are usually expected to be dependent. Indeed, it is this dependence from one time period to another which will be exploited in making reliable forecasts.... It also will be useful to distinguish between a time series process and a time series realization. The observed time series is an actual realization of an underlying time series process. By a realization we mean a sequence of observed data points and not just a single observation. The objective of time series analysis is to describe succinctly this theoretical process in the form of an observable model that has similar properties to those of the process itself. (p. 3).... A time series model consisting of just one variable is appropriately called a univariate time series model. A univariate time series model will use only current and past data on one variable..... A time series model which makes explicit use of other variables to describe the behavior of the desired series is called a multiple time series model. The model expressing the dynamic relationship between these variables is called a transfer function model. The terms transfer function model and multiple time series model are used interchangeably. (p. 8).... Finally, a special form of transfer function model is the intervention model. The special characteristic of such a model is not the number of variables in the model, but that one of the explanatory variables captures the effect of an intervention, a policy change, or a new law. (p. 9).

The use of intervention analysis to evaluate remaining discharge data might be particularly appropriate providing that adequate data quality exists. One of the seminal works in intervention analysis is described in Tiao and Box and Hamming (1973) and Box and Tiao (1975) in which photochemical smog data from Los Angeles was analyzed in order to evaluate the effect of a new law requiring the reduction of reactive hydrocarbons upon the oxidant pollution level in the city. This is analogous to analyzing abandoned mine drainage pollution load data collected before, during and after remaining in order to determine the effect of remaining upon the level of the baseline pollution load in the presence of significant seasonal variations. An example of the use of intervention analysis of abandoned mine drainage data is the study by Duffield (1985) of the Arnot discharges, that are also featured in Chapter 4 of this report.

According to Box and Tiao (1975, p. 70):

Data of potential value in the formulation of public and private policy frequently occur in the form of time series. Questions of the following kind often arise: “Given a known intervention, is there evidence that change in the series of the kind expected actually occurred, and, if so, what can be said of the nature and magnitude of the change?” ... In the examples quoted, however, the data are in the form of time series, in which successive observations are usually serially dependent and often nonstationary and there may be strong seasonal effects. Thus, the ordinary parametric or nonparametric statistical procedures which rely on independence or special symmetry in the distribution function, are not available nor are the blessings endowed by randomization.

Intervention analysis and other methods of time series analysis are very powerful statistical tools which would be desirable and useful in evaluating baseline pollution load data, but these types of statistical analyses will usually be inappropriate for remaining permitting due to inadequate data availability and data quality. Therefore, it was necessary to develop a data analysis algorithm which recognized or allowed for the use of time-series analyses, but did not require the routine use of these statistical methods in order to answer the desired questions about the remaining discharge data.

A flow chart outlining the data analysis algorithm for determining the baseline pollution load is shown in Figure 3.1. The algorithm includes evaluations of data quality, univariate statistical analyses, bivariate statistical analyses and time series analyses methods to establish quality control limits. The algorithm includes steps to evaluate the normality of the frequency distribution and transform the data if the distribution is not normal (i.e., positively skewed); however, the use of the statistical methods in the algorithm does not require the distribution to be normal. The algorithm contains elements of parametric statistical analysis, but it is primarily based upon order statistics and non-parametric statistics.

Chapter 3: Mine Drainage Data Analysis Algorithm

A flow chart outlining the data analysis algorithm for determining baseline pollution load is shown in Figure 3.1. The algorithm includes evaluations of data quality, univariate statistical analyses, bivariate statistical analyses and time series analyses. The algorithm also includes steps to evaluate the normality of the frequency distribution and logarithmically transforms the data if the distribution is not normal (i.e., positively skewed); however, the use of the statistical methods in the algorithm does not require the distribution to be normal.

All of the statistical analyses included in the algorithm are contained in the MINITAB¹ computer software package, which was used to assess the data presented in this report. The analysis contained in MINITAB was incorporated into the REMINE² computer software package developed by EPA, PA DEP, and Pennsylvania State University. Other software packages included Statistical Analysis Software (SAS) and Stat Graphics. A significant feature of the algorithm and the MINITAB program in general is that a user with limited statistical analysis experience can perform the rudiments of the baseline pollution load analysis without encountering too much difficulty, while the user with greater statistical training can expand the statistical analysis to include a much greater array of statistical methods if desired. The remainder of this chapter is devoted to explaining the elements of this remaining data analysis algorithm.

Data from six study sites were submitted to the standard procedures shown in Figure 3.1. (These data are described in detail in Chapters 4 through 8.) There are twelve steps in the complete analysis, and it should be emphasized that only the first nine are needed for routine reminging permits. Steps 11 and 12 are for research purposes only. The most important step is initial examination of the data (Step 1, Figure 3.1). Following this examination, missing values are identified and adjusted. Additionally, any extreme outliers (Step 3) should be examined to see if they are real observations or errors of entry at some stage in the data collection procedure.

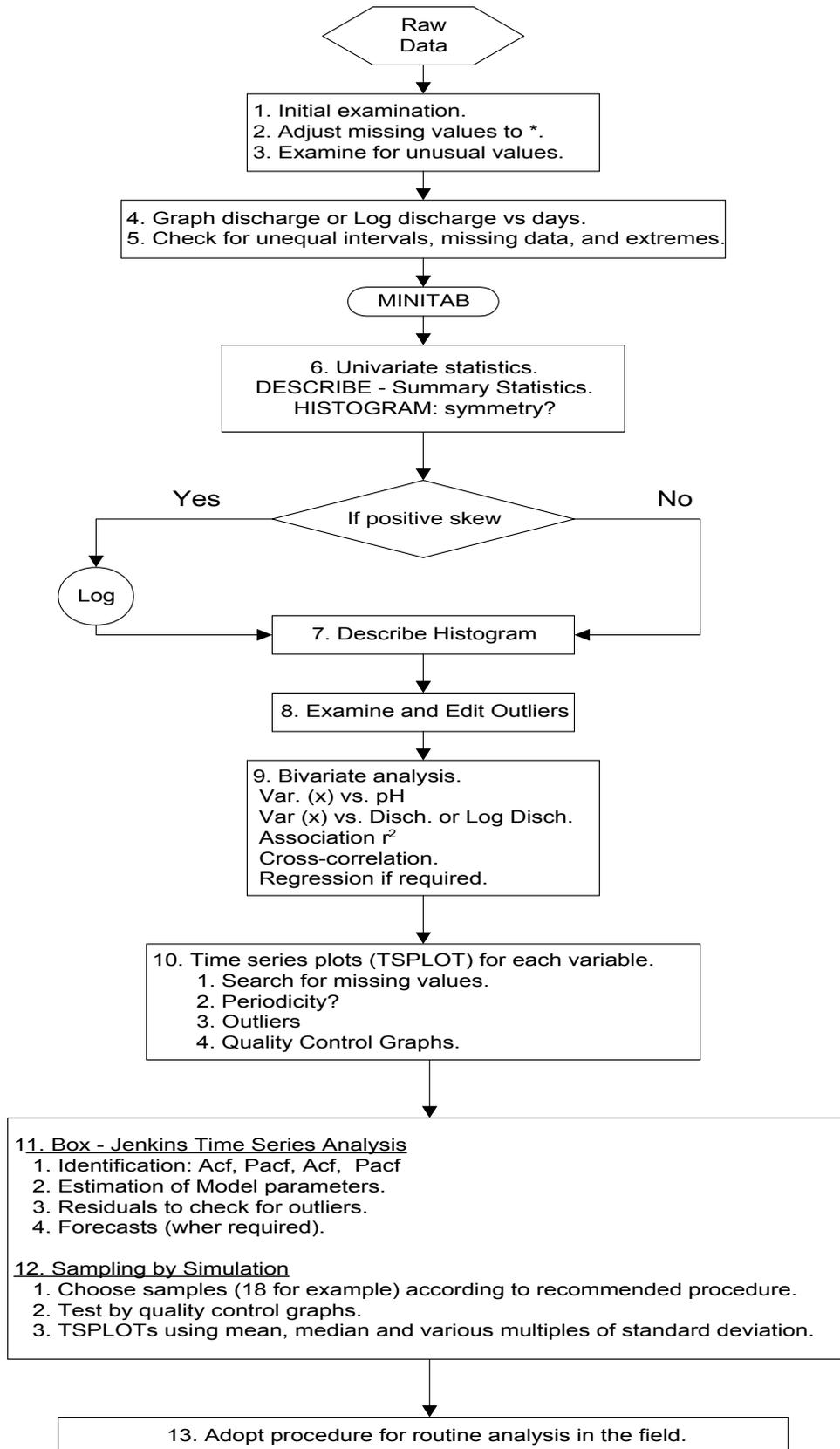
The next step (Step 4) is to graph discharge (flow) versus days (ordered observations). Frequently, it is advisable to plot log discharge in order to reduce extreme variations. This procedure also helps to reduce extreme positive skewness (if present in the data). This reduction of asymmetry improves the subsequent analysis of the data and makes the probability statements more reliable. Because extreme observations may result from unusual events (such as heavy downpours, snowmelt), the reduction of variation should be used with discretion. In many cases, these unusual extreme data values may indicate events of considerable importance in the study of the natural variation in the data.

¹MINITAB is a commercial software package from Minitab, Inc. ©1986, 3081 Enterprise Drive, State College, PA 16801.

²REMINI is a computer software package developed by EPA, PA DEP and the Pennsylvania State University, Version 1.0 (November 1988) and Version 2.0 (April 1992), page R-2.

Step 5 is also crucial for determining regularity of the sampling to further identify the larger gaps in the data. The plot of discharge versus days prepared in Step 4 is one way of seeing this aspect of behavior in the data. Another useful procedure is to take “first differences” of days (or order of observation). This procedure leads to a frequency distribution and a histogram in which the intervals between observations are clearly displayed.

Figure 3.1 Algorithm for Analysis of Mine Drainage Discharge Data



Ideally, all the intervals between the observations should be equal; in practice, this is rarely achieved. One or two days on either side of the ideal date is adequate for fourteen-day intervals. Many gaps of five or six days make the subsequent analysis much less exact and larger intervals (e.g., 90 days) make the analysis more difficult to interpret correctly. Large gaps in the data preclude rigorous time series analysis which requires a very close approximation to equal intervals between observations. In general, the more sophisticated the statistical analysis, the more sensitive it is to data gaps.

As a general recommendation, it is helpful to insert a missing data symbol (e.g., *) where there are data gaps (i.e., a few missing flow measurements or a few missing values for water quality parameters) and produce the mean, median, standard deviation, etc. of the truncated data set. If the frequency distribution of the variable is reasonably representative (e.g., symmetric), or has been made so by log transformation, then the means may be substituted for each missing data symbol (*) and the frequency distribution and summary statistics (mean, median, standard deviation) rerun on more complete data. Of course, insertion of the mean does not gain information; it only makes subsequent analysis more correct. If the data are asymmetric, the median is a more representative estimate of the “central tendency” and should be used rather than the mean.

This entire procedure (Steps 1–5, Figure 3.1) is aimed at “massaging” the data into a form suitable for statistical analysis. If there are only a few observations (18 or so, for example) it is somewhat arbitrary whether or not one wishes to smooth the data, because very little extended analysis will be appropriate.

Univariate Analysis (Algorithm Steps 6, 7, and 8)

In Step 6, the data are analyzed and plotted to obtain the summary statistics and to examine graphical displays of the data to determine the presence of skewness and extreme values. Stem and Leaf plots can be used in place of histograms of frequency distributions as shown in Figure 2.4.

This procedure includes calculating statistics for each individual variable (univariate statistics). An example of this procedure is displayed in Table 3.1 of the summary statistics for the analysis of the data from the Clarion site (discussed in Chapter 5). In this example, there are seven parameters and eleven summary statistics that were calculated using the REMINE program. There are $N = 96$ observations (column 1 of Table 3.1); N^* (column 2) is the number of missing observations (19 for the discharge variable). Columns 3 and 4 list the means and medians respectively. Column 5 is a special kind of mean, called by Tukey (1977, p. 46) the “trimmed mean.” Columns 6 and 7 contain the standard deviation (STDEV) and standard errors (SEMEAN) of the mean as measures of spread. Columns 8 and 9 list two extremes (min and max) yielding the range of the values. Columns 10 and 11 contain the quartiles (Q_1 and Q_3), yielding a measure of spread around the central tendency (mean or median); this spread is less sensitive to the extremes and so is often preferred in distributions which are irregular (e.g., strongly skewed). The coefficient of variation (Column 12), usually expressed in percent (CV%), is defined as the ratio of the standard deviation to the mean multiplied by 100. This is a

useful approximate guide to the degree of variation in a parameter. In general, a CV < 30% represents a stable (in control) parameter. Most of these parameters, however, show much larger variation, principally because of the large effects of extreme events.

Table 3.1: Summary Statistics for S3CLAR (N=96)

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
pH	96	0	3.696	3.195	3.612	0.985	0.101
Discharge	77	19	12.58	6.30	9.00	22.66	2.58
Acidity	96	0	522.4	483.5	505.6	346.4	35.4
Total Iron	96	0	82.40	75.00	79.31	51.01	5.21
Ferrous Iron	96	0	54.84	39.50	47.44	66.99	6.84
SO ₄	96	0	1528.	1569.0	1525.9	566.0	57.8
Ferric Iron	96	0	27.56	23.60	31.01	70.58	7.2

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	2.670	6.430	3.002	4.455	26.6
Discharge	0.05	172.00	3.59	12.54	188.1
Acidity	1.0	1546.0	232.5	737.7	66.3
Total Iron	8.70	257.00	39.70	110.25	61.9
Ferrous Iron	0.90	612.18	25.12	68.60	122.2
SO ₄	296.0	3241.0	1181.5	1878.2	37.0
Ferric Iron	-581.68	152.00	5.00	55.00	256.1

A second series of statistics referred to as letter values (e.g., H-spread) is sometimes calculated to identify various measures of spread. These spreads can be used to set limits for water quality (see Tables 8.6 and 8.7, (Q₃-Q₁)). These letter values (LVALS) were first defined by Tukey (1977, p. 22) and are mentioned in the MINITAB Reference Manual (p. 168). These values are best described in Velleman and Hoaglin (1981, p. 33).

If the data are positively skewed (i.e., skewed towards the high end of the values on the variable scale) the data should be logarithmically transformed and the univariate analysis repeated (Step 7, Figure 3.1). The log transformation tends to make the histogram more symmetrical, although there is a tendency to over-correct in some cases and introduce negative skewness.

It is possible to use another transformation such as the square root of the variable, which may well suffice to avoid over-correction that came from the logarithmic change. The use of various transformations is reviewed in Tukey (1977, Chapter 3) and specifically for symmetry, in the MINITAB Handbook (p. 72 – 76) and the MINITAB Reference Manual (p. 50 – 52). It is also discussed in Velleman and Hoaglin (1981, p. 46 – 49) and Box and Cox, (1964).

In evaluating the statistics produced for the transformed data, the user should be cautious of the coefficient of variation values. Use of the coefficient of variation with log transformed data may result in extreme distortion because the transformation leads to a mean of small value. This results in a denominator of the ratio that is small resulting in a CV that is inflated.

Step 8 in Figure 3.1 is used to check and accept or modify outliers. Outliers tend to inflate the variance or spread of the data and make the statistical tests less sensitive. For this reason, outliers should be reduced only after deciding that such extreme values are not “real” or when it is specifically desired to make the statistical testing more sensitive. As mentioned earlier, some outliers are indicators of unusual events (e.g., floods, storms) and should not be removed or even subdued, but instead should be used to reflect the occasional unusual events.

Bivariate Analysis

The next step in data analysis (see Step 9) concerns the relationship between pairs of variables (bivariate analysis). If two variables are closely associated (e.g., a correlation coefficient, $r > 0.8$), both may be reflecting the same source of variation and one may be considered redundant. It is possible to use this kind of feature to select the simpler test (or less expensive analyte) and ignore the other parameter in subsequent studies. Sometimes several variables reflect the effects of the same events.

One expects, for example, pH to decline with increasing acidity and sulfate. In the case of calcium and manganese, on the other hand, one expects sympathetic variation. If examination of the data shows that this expected relationship is not present, the reason for its absence should be sought.

The correlation coefficient (r) is usually used to represent the (linear) relationship between any pair of variables. The coefficient of determination (r^2) is, however, a better measure of the intensity of the association between a pair of variables; for example, $r = 0.7$ looks large because the range of r is from -1 to $+1$, but it means that $r^2 = 0.49$ or 49% of the variation is common to the two variables and there is 51% of the variation “unexplained” by the association. It is necessary, therefore, to realize that one needs $r > 0.8$ to claim that a strong association exists (i.e., $> 64\%$ in common).

Another feature which is illuminated by using r^2 as well as r is the statistical test which accompanies a specific value of r . For a sample size of $N = 174$ (Table 6.3), a value of $r > 0.124$ is significantly different from zero at the five percent probability level. This should be accompanied by the corresponding value of r^2 . In Table 6.3, the correlation coefficient between pH and acidity is $r = -0.365$. This value comfortably exceeds the $r = (\pm) 0.124$, thus it is statistically significant. Nevertheless, the corresponding $r^2 = 0.133$ means that only 13.3% of the variation is common to both variables.

In the graphs presented in Figures 6.5a and 6.5c, the variation of both parameters increases as their values increase. This phenomenon is called heteroscedasticity. In general, it is advisable to plot the logs of the variables which tends to make the variables homoscedastic. Since

heteroscedastic variables show a difference in variability with changes in values of the parameter, no probability statement should be made without transformation so that the variables are homoscedastic. Peculiarly, the change from heteroscedasticity to homoscedasticity does not lead to a major change in the value of r , but does make the probability statements more reliable.

One more avenue should be explored in bivariate analysis, and that is to determine whether there is any lag in correlations between pairs of variables. Cross-correlation analysis is performed to see if a weak relationship at zero lag may be much stronger at greater lags. This could result from a delayed effect. For example, suppose discharge increases and sometime later, pH drops. Correlation at zero lag may be quite low, but at some higher lag it may increase showing that it takes time for the effect of changes in discharge to affect pH or some other variable. The cross-correlation function (CCF) is the measure used for this purpose. For example, suppose that an event occurs and affects one variable immediately but only affects another variable five observations later. In this case, the linear correlation coefficient at zero lag may be quite low but may show a strong association after a five day lag. The cross-correlation function calculates the linear association between observation 0 to t days apart and so gives a picture of when the association is strongest. The range of t is from $-(\sqrt{N} + 10)$ to $(\sqrt{N} + 10)$ where N is the number of observations in the series. In most of the examples presented in this report, there did not appear to be any lag in the effects.

Time Series Analysis

The remaining steps (10 through 12, Figure 3.1) were used to set up baseline behavior based on relatively long data records. In this way, expected behavior of various parameters are established for comparison with the shorter data records that are commonly used in routine remining permitting. The likelihood of unusual events is then displayed, and the frequency of a single or a few unusual observations may be used to judge how often these events occur. In this way, these events can be distinguished from other departures that lead to warnings, triggers, or exceedances in pollution load and therefore, would be less likely to result in false alarms.

One procedure which is readily available as part of the full Box-Jenkins treatment, but was not used in these studies, was Transfer Function analysis. This analysis would be a most attractive way to correct variation in some parameter (e.g., Fe) for variation in flow and then proceed to analyze the residual variation in the parameter after the effects of flow were removed. This would also be an alternative way of looking at the “load” variable in place of concentration.

Similarly, there is a procedure in Box-Jenkins analysis called “intervention analysis” which may be used to compare and contrast variation in a parameter before and after treatment is applied. This has obvious applications to remining operations. Needless to say, use of these procedures requires an extensive set of observations taken at equal intervals, with few data gaps.

Variation in many of the parameters, from the different locations, appears to follow a common pattern. There is usually some type of gradient present in the data which may be increasing or decreasing over time. This results in a typical autocorrelation function (Acf) pattern and a large spike at lag 1 in the partial autocorrelation function (Pacf). This trend should be removed before

fitting a model. This is best done in nearly all the examples in this particular series of investigations by taking first differences of the variable of interest. The subsequent model-fitting usually leads to a moving average model. In Box-Jenkins notation this is an IMA (0,1,1) model. It is essentially a random walk after first differences are taken.

Quality Control (QC) Limits

Step 10 of the algorithm on times series plots of the variables (Figure 3.1) includes an item (# 4) on quality control graphs. Items 2 and 3 of Step 12 (sampling by simulation) also refer to quality control graphs. The final step of the algorithm (Step 13) is a procedure for routine statistical analysis of data contained in remining permits. From the discussion of quality control throughout Chapter 2, it is obvious that the development of a relatively simple quality control approach for mine drainage data analysis is a major objective of this report and a significant component of the routine procedure in Step 13 of the algorithm. Chapters 4 through 8 contain further discussion, tables and plots of various examples of quality control limits. Examples from the six mine drainage case study sites lead to the statistical summary and review of quality control limits in Chapter 9, wherein options for the routine use of quality control limits are presented.

Throughout this report the conventional quality control limits based upon the mean and standard deviation of the normal frequency distribution are compared to another set of non-parametric quality control limits based upon the median and other order statistics (e.g., quartiles, H-spreads, C-spreads), which may be more applicable to mine drainage data that frequently do not conform to normality. The quality control options in Chapter 9 of this report are a component of the routine procedures for establishing baseline pollution load and monitoring in remining permits. These procedures are related to the recommended statistical procedures set forth in Chapter 3 and Appendix A of EPA's *Coal Remining Statistical Support Document*. However, the user of these routine procedures should be ever mindful that no single set of quality control limits or specific statistical test will be perfectly applicable to all mine drainage sets or even to all discharge parameters within the same data set. The user should carefully examine the data and follow the fundamental steps of the algorithm in order to properly use the statistical tools that are most applicable to the characteristics of the data.

In the following chapters, more than one equation was used to calculate QC interval spreads. These equations were chosen based on the distributions of the parameters collected in the given data sets (i.e., number of results, amount of variability, lack of normality, etc.)

The first equation ($\bar{X} \pm 2\hat{\sigma}$) is based on the typical confidence interval for a mean under the normal distribution. However, unlike the typical equation for a confidence interval around a mean, the standard deviation was not divided by the square root of the number of results (N). The exact interpretation of the usual confidence interval is that the true mean of all post-remining results for the given site will fall into the calculated interval with 0.95 probability. For the purpose of quality control, however, this interval may be extremely tight, given the large number of results collected for each dataset. For baseline permit pollution load data sets, the number of results collected would likely be much less, and therefore would produce wider

intervals. A different value of N (N') could be used in the equation, reflecting the number of results likely to be collected and used to calculate the mean that will be compared to the interval. For example, if monthly samples are collected for a year, N' would equal 12. However, if the purpose of the interval is to evaluate individual results rather than a mean, then N' should equal 1. This is what was done in Chapters 4, 6, 7 and 8, where the above equation is used.

The two other equations that are used in quality control tables in the following chapters are non-parametric, in that they do not require that the collected data follow a normal distribution. They are based on the non-parametric equivalent of the mean (the median) and the non-parametric statistic for variability (the interquartile range). The first interval,

$$Md \pm 1.96 * \left(\frac{1.25 * H - spr.}{1.35 * \sqrt{N'}} \right),$$

is discussed in McGill, Tukey and Larsen (1978). This interval is used to assess whether a median follows the same population as the baseline pollution load data, and is therefore divided by the square root of N', where N' is the expected number of remaining results. The chosen multiplier, 1.96, is appropriate when it is assumed that the variability of the baseline data and the remaining data are approximately equal. However, if the variability of the baseline data and remaining data are different, a smaller multiplier (1.39) is appropriate. When it is not known whether the two variances will differ, the midpoint of 1.39 and 1.96, (i.e., 1.7) could be used. The above equation is used in Chapters 6, 8 and 9.

A second equation, $Md \pm 1.58 * (H - spr.)$, was used in Chapter 4. In this second equation, the value of 1.58 was chosen by using the midpoint multiplier (1.7) and simplifying the equation by multiplying by 1.25 and dividing by 1.35. The purpose of this equation differs from the previous one, in that it is designed to evaluate individual results, rather than the remaining median.

Chapter 4: Analysis of Data from the Arnot 001, 003 and 004 Discharges

The Arnot mine site is located in Tioga County, Pennsylvania in the northeastern portion of the bituminous coal region. The Arnot discharges are from an abandoned underground mine on the Bloss (B) coal seam, which is the subject of a hydrogeologic study by Duffield (1985). The relationships between flow and water quality parameters of the Arnot mine site are also described in Smith (1988) and Hornberger et al. (1990). A map of the Arnot site is shown in Figure 4.1. The data set for the Arnot site contains 82 samples from each of the 3 mine drainage discharges for the time period from January 28, 1980 to August 14, 1983.

It is advisable to examine the distribution of the missing values because they will lead to difficulties as the analytical (statistical) tools get more sophisticated. In particular, time series analysis demands observations at regular time intervals. On the other hand, it is impractical to expect that there will be no missing values, because during a storm event, the sampling location may become inaccessible for various time intervals. It is best, therefore, to recommend time interval limits for the period in which a sample may be taken, and which, for statistical analysis, will be considered to be within the time interval (e.g., any time within a two week period will be assigned as an observation taken 2 weeks apart at the mid-point of the time interval). In any case it is advisable to examine the data carefully before attempting a quantitative analysis. Therefore, it is recommended that a graph of discharge (and/or other variables) against time be prepared and examined carefully to determine the distribution of missing values, position of the extremes, etc.

A typical example is illustrated in Figure 4.2 which is a plot of log (base 10) of flow versus time for all three point sources from the same mine. The flow for Arnot 001 is usually the largest followed by Arnot 004, then Arnot 003. All three show the same general pattern of variation.

The samples were supposed to be taken at 14 day intervals but, in practice, the intervals vary from 1 day up to 40 days. All intervals equal to or exceeding 20 days are accented in Figure 4.2. These longer intervals include, of course, many missing values. When a time series model is fitted to these data, they are "forced" into equal interval status. The effect of these departures from equal intervals is to suppress any seasonal periodicity that may be present.

It may be observed that in 1980 the runoff occurred in March, April and May; in 1981 in March and April; in 1982 in March and June; and in 1983 in April and May. These variations tend to suppress any seasonal effect in the occurrence of extreme values.

Figure 4.1: Map of Arnot Mine Site

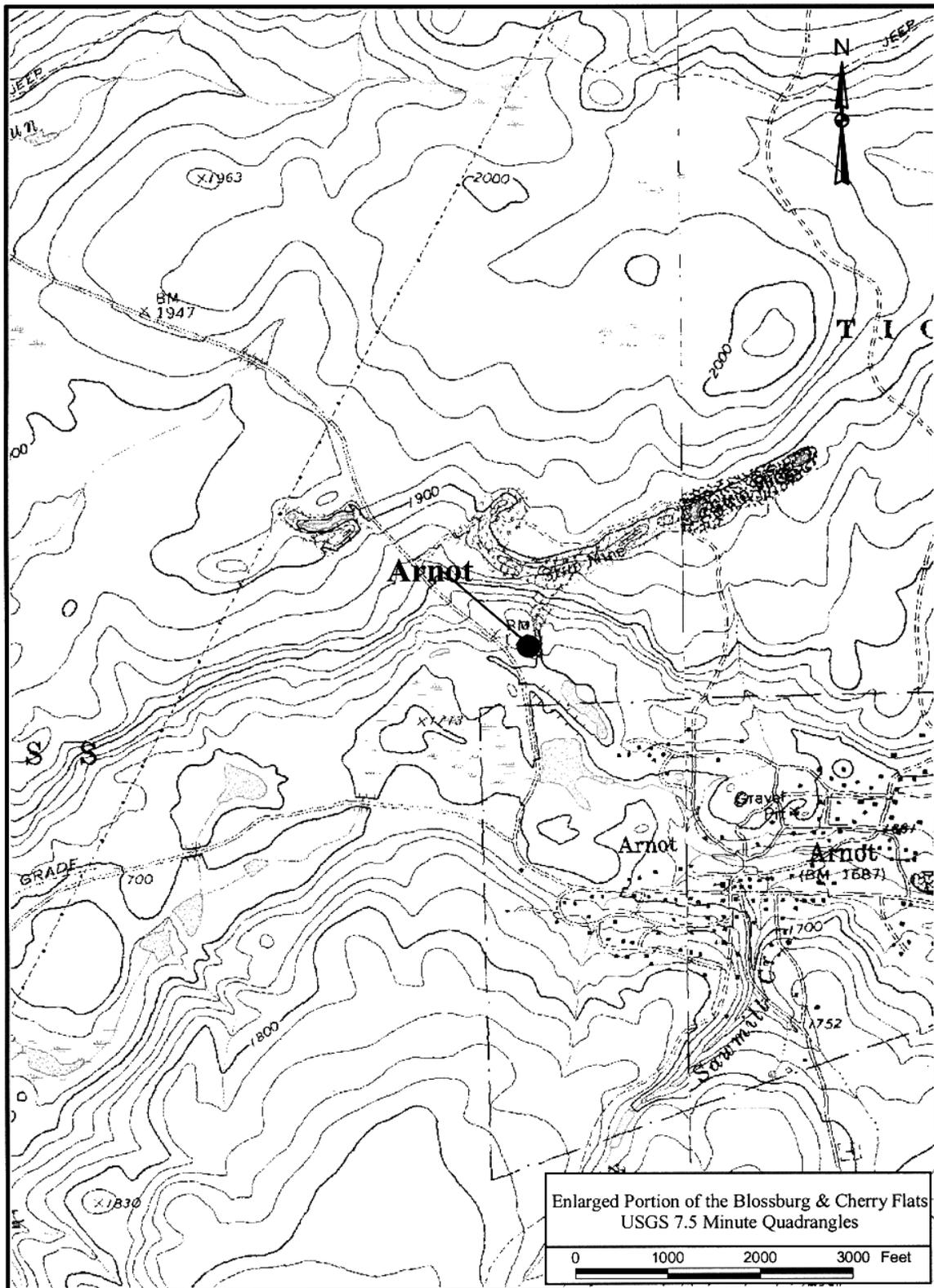
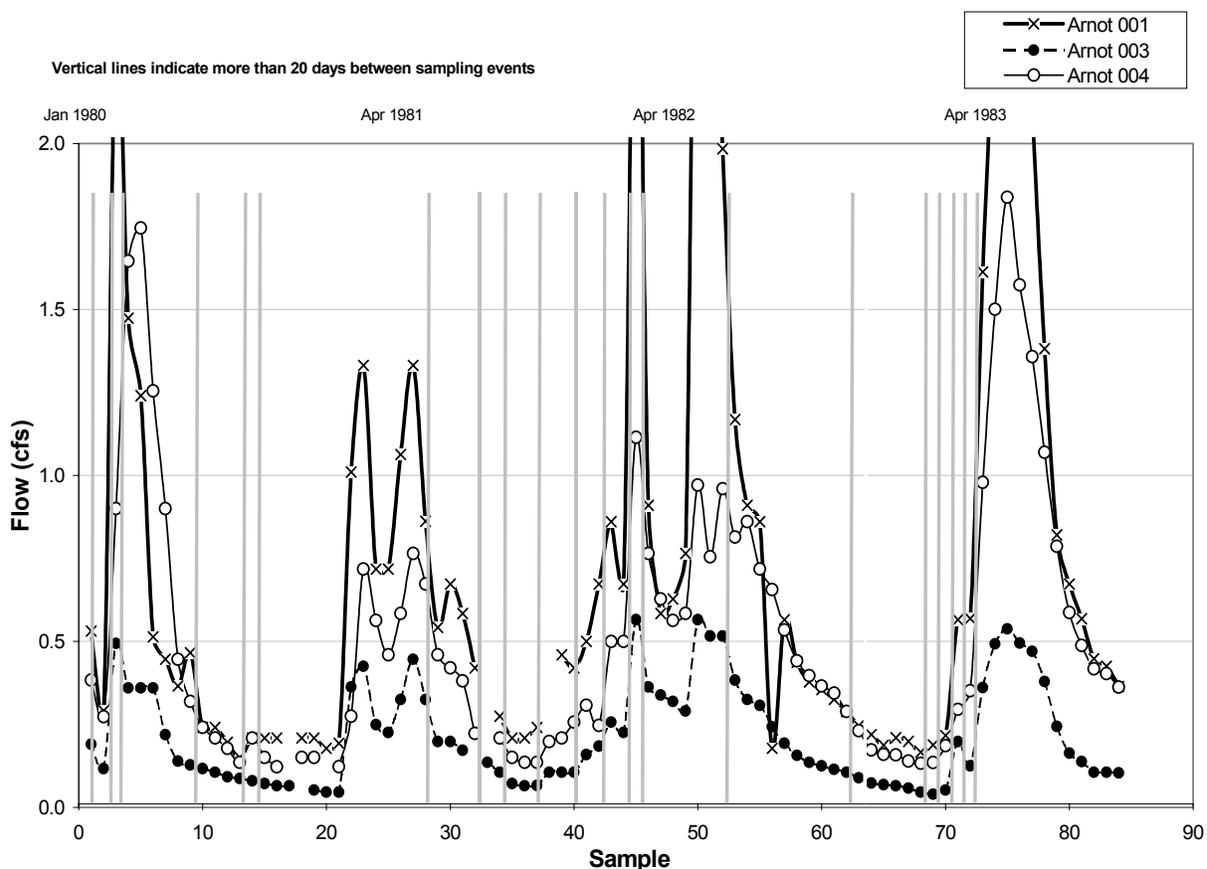


Figure 4.2: Log Flow vs. Time (Arnot 001, 003, and 004) Procedures to Adjust the Data Set for Missing Data



In some cases, it will be advantageous to insert some suitable value in place of the missing observation and the procedures for selection of a suitable value can differ. One such approach is to insert the mean value for the series or, if the frequency distribution is somewhat skewed (asymmetric), the median may be more representative.

There are also smoothing procedures varying from simple ones, such as the average of a pair of values on either side of the missing observation, through running averages using any of several larger sets of numbers. These, smoothing procedures, are described in Velleman and Hoaglin (1981, Chapter 6) and (Cleveland, 1979).

A typical, but rather elaborate example, specifically designed for time series analysis, is described by Damsleth (1986). This example begins with “simple linear interpolation between observations preceding and following the gap” then identifying and estimating a univariate time series model for the “adjusted series” which, in turn, yields “optimal estimators using the model.” The new series is used to build a transfer function model between two series (such as acidity and flow) and calculating new optimal values which are in turn used to estimate new

model parameters (Damsleth, p. 46-47). The conclusions reached by Damsleth (p. 47) are: “The various steps in the process gave only small changes in the estimates for missing values, and the model and parameter estimates were almost unaffected....”.

It should be clear that missing observations can be a very difficult problem. Another aspect of this “data massaging” procedure arises when attempts are made to reduce the magnitude of the error of residuals when fitting a time series model. In a series of flow observations, for example, there may be some extremely large values that arise from unusual events (e.g., heavy rainfall, perhaps persisting for several days, sudden water run-off from snow melt, etc.). These “natural” events of limited duration can increase the residual error quite seriously and usually do not represent persistent increased contamination. In the series of mine drainage data examined in this chapter, these unusually large values are often associated with missing data. This means that if one inserts a very small value (near zero) for the missing value, the entire range in parameter values occurs within a short period. It is advisable to reduce this wide range, first by not using low values for zero or missing values but by using one of the procedures described above. Secondly, the extreme high values should be smoothed out (i.e., large variance, and wide confidence limits which tend to be insensitive to large departures in the data). The effects of these adjustments may be estimated by running the series, after removing the zero values, both with the original extreme values and with the extremes adjusted by some form of smoothing.

In comparing the results of the more sophisticated smoothing technique described by Damsleth with other “quick and dirty” techniques, it was found that the changes were not very different. Therefore, it was concluded that elaborate smoothing procedures are unnecessary for mine drainage data sets.

Univariate Analysis

The analysis commences with the summary statistics displayed in Tables 4.1a to 4.1c. The number of samples (N) for each variable is listed first, followed by the number of missing values (N*). The statistical summary then follows with values for the arithmetic mean, median, trimmed (10%) mean, standard deviation, standard error of the mean, minimum, maximum, and the first and third quartiles. A convenient procedure for comparing variabilities among different variables, and among the same variables from different sources, is by means of the Coefficient of Variation (CV) where $CV\% = (\text{standard deviation} / \text{mean}) * 100$ expressed in percent. The values are displayed in Table 4.2 for convenient comparisons. For all three Arnot sources, pH has the smallest variability (around 4%), whereas, discharge has the largest variability (Arnot 1: CV=112%, Arnot 3: CV=70.0%, Arnot 4: CV=78.1%).

Table 4.1a: Summary Statistics for Arnot 001 Data

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
pH	81	0	4.8505	4.8400	4.8479	0.2221	0.0247
Temperature	67	14	9.448	9.100	9.403	1.424	0.174
Discharge	81	0	0.7961	0.5000	0.6747	0.8955	0.0995
Acidity	81	0	20.04	16.00	19.42	11.26	1.25
Alkalinity	81	0	6.457	5.000	5.918	5.480	0.609
Total Iron	81	0	0.21111	0.20000	0.21096	0.07583	0.00843
Ferrous Iron	81	0	0.11728	0.10000	0.11507	0.07872	0.00875
SO₄	81	0	173.23	177.00	173.22	44.05	4.89
Ca	75	6	109.52	111.00	109.73	22.76	2.63
Mg	75	6	86.03	82.00	85.76	24.87	2.87
Mn	75	6	1.7104	1.6200	1.6776	0.6666	0.0770
Al	72	9	1.425	1.045	1.384	0.982	0.116

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	4.2000	5.4500	4.6800	5.0200	4.5
Temperature	7.000	12.900	8.400	10.000	15.1
Discharge	0.0100	5.0910	0.2300	0.8615	112.0
Acidity	3.00	64.00	11.00	28.00	56.2
Alkalinity	0.000	37.000	3.000	8.000	84.8
Total Iron	0.00000	0.40000	0.20000	0.25000	35.9
Ferrous Iron	0.00000	0.30000	0.10000	0.20000	67.1
SO₄	66.00	277.00	140.50	201.50	25.4
Ca	66.00	152.000	93.00	127.00	20.8
Mg	31.00	145.000	69.00	104.00	28.9
Mn	0.5400	3.9500	1.2800	2.0300	39.0
Al	0.100	3.640	0.602	2.277	68.9

Table 4.1b: Summary Statistics for Arnot 003 Data

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
pH	82	0	3.2782	3.265	3.2727	0.1095	0.0121
Temperature	67	15	8.551	8.600	8.548	0.916	0.112
Discharge	82	0	0.2157	0.1610	0.2671	0.1509	0.0167
Acidity	82	0	86.37	84.50	85.7	22.55	2.49
Total Iron	82	0	1.0963	1.1000	1.0919	0.2843	0.0314
Ferrous Iron	82	0	0.3610	0.3000	0.3405	0.2340	0.0258
SO₄	82	0	168.99	165.00	168.66	43.79	4.84
Ca	75	7	59.75	61.00	59.52	11.69	1.35
Mg	75	7	73.60	70.00	72.49	23.00	2.66
Mn	77	5	3.203	2.760	3.110	1.338	0.152
Al	73	9	5.079	4.680	5.060	2.213	0.259

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	3.0400	3.7000	3.2100	3.3325	3.3
Temperature	6.200	11.700	8.100	9.000	10.7
Discharge	0.04	0.5650	0.1010	0.3282	70.0
Acidity	42.00	151.00	67.75	104.00	26.1
Total Iron	0.3000	2.0000	0.9000	1.2000	25.9
Ferrous Iron	0.0000	1.5000	0.2000	0.4000	64.8
SO₄	85.00	262.00	134.00	211.25	25.9
Ca	38.00	90.00	49.00	69.00	19.5
Mg	38.00	142.00	55.00	89.00	31.2
Mn	1.540	6.900	2.040	4.350	41.7
Al	0.700	9.440	3.400	6.960	43.6

Table 4.1c: Summary Statistics of Arnot 004 Data

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
pH	81	0	3.2794	3.2800	3.2675	0.1409	0.0157
Temperature	67	14	8.466	8.600	8.487	0.906	0.111
Discharge	81	0	0.5307	0.4030	0.4887	0.4143	0.0460
Acidity	81	0	96.99	96.00	95.85	26.61	2.96
Total Iron	81	0	1.2630	1.200	1.243	.418	0.0464
Ferrous Iron	81	0	0.4198	0.3000	0.3973	0.2638	0.0293
SO₄	80	1	171.80	166.50	170.79	39.04	4.36
Ca	75	6	54.293	54.000	54.164	8.022	0.926
Mg	75	6	67.68	65.00	67.27	18.52	2.14
Mn	75	5	2.714	2.445	2.637	0.979	0.112
Al	73	8	6.453	5.900	6.317	2.590	0.303
Log Discharge	81	0	-0.3954	-0.3947	-0.4024	0.3266	0.0363
Ferric Iron	81	0	0.843	0.800	0.845	0.382	0.043

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	3.0000	3.9400	3.1900	3.3350	4.3
Temperature	6.100	10.700	8.100	9.000	10.7
Discharge	0.1220	1.8380	0.2090	0.7365	78.1
Acidity	62.00	168.00	73.00	121.00	27.4
Total Iron	0.600	2.8	0.900	1.500	33.1
Ferrous Iron	0.0000	1.4	0.2500	0.5000	62.8
SO₄	86.00	268.00	143.00	200.00	22.7
Ca	39.000	79.000	49.000	60.000	14.8
Mg	17.00	110.00	54.00	75.00	27.4
Mn	1.200	6.500	1.987	3.247	36.1
Al	0.710	13.560	4.325	8.350	40.1
Log Discharge	-0.9136	0.2643	-0.6799	-0.1330	82.6
Ferric Iron	0.000	1.700	0.600	1.100	5.1

Table 4.2: Coefficient of Variation (%)

Variable	Arnot 001	Arnot 003	Arnot 004
pH	4.5	3.3	4.3
Temperature	15.1	10.7	10.7
Flow	112.0	70.0	78.1
Log (Discharge)	-	-	82.6
Acid	56.2	26.1	27.4
Alkalinity	84.8	-	-
Total Iron	35.9	25.9	33.1
Ferrous Iron	67.1	64.8	62.8
Ferric Iron	-	-	5.1
SO ₄	25.4	25.9	22.7
Ca	20.8	19.5	14.8
Mg	28.9	31.2	27.4
Mn	39.0	41.7	36.1
Al	68.9	43.6	40.1

The same CV order of magnitude is maintained by each variable in each of the three sources. Log discharge does nothing to reduce the relative variation (CV) as can be seen from the value for Arnot 004 (82.6%). Discharge is highest in Arnot 001, moderate in 004, and lowest in 003. The coefficient of variation reflects this order and suggests that this parameter varies in proportion to its absolute value (heteroscedastic), again reinforcing that the appropriate transformation is to logarithms.

The majority of the variables in the histogram-like displays of data from Arnot 001 are symmetrical, such as sulfate shown in Figure 4.3. The most asymmetric is discharge which is seen in Figure 4.4. When this variable is transformed to logarithms it becomes symmetrical.

Figure 4.5: Stem-and-leaf of pH (Arnot 003)

N = 82
 Leaf Unit = 0.010

1	30	4
2	30	7
5	31	134
17	31	555667888999
36	32	00111111112234444444
(15)	32	555666777789999
31	33	001111222234
19	33	556666778
10	34	1122
6	34	679
3	35	0
2	35	7
1	36	
1	36	
1	37	0

Figure 4.6: Stem-and-leaf of Sulfate (Arnot 004)

N = 80
 Leaf Unit = 1.0 N* = 1

1	0	8
3	11	00
16	1	22223333333333
33	1	444444444444555555
(18)	1	666666666666667777
29	1	88888999
21	2	00000111
12	2	2222233
5	2	455
2	2	66

Figure 4.7: Stem-and-leaf of Acidity (Arnot 004)

Figure 4.7 : Stem-and-leaf of Acid.

N = 81

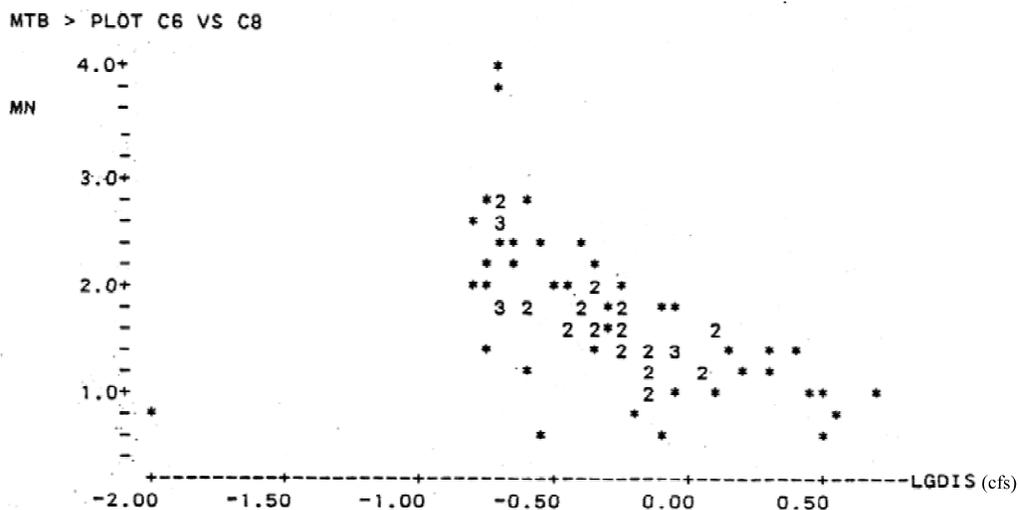
Leaf Unit = 1.0

13	6	2444456677799
32	7	0011223333445677899
38	8	001238
(6)	9	256778
37	10	0000337
30	11	112245558
21	12	112445678
12	13	01123677
4	14	05
2	15	2
1	16	8

Bivariate Analysis

The relationships between log discharge and every other parameter are similar (i.e., inverse and approximately linear). That is, as discharge increases in volume the amount of each variable, calcium, magnesium, manganese and aluminum, decreases, or in high flows the concentration is diluted. A good example of this relationship is the plot of manganese versus flow for the Arnot 001 discharge, shown in Figure 4.8.

Figure 4.8: Plot of Manganese vs. Log Flow (Arnot 001)



For Arnot 003, acidity vs. discharge possesses a clear, curvilinear association (Figure 4.9), which would become inversely linear if discharge was expressed in logs. Cross-correlation of these variables had maximum association of -0.648 at zero lag, or about 42% of the variation (r^2) is common to both variables. Sulfate, manganese and aluminum vs. discharge also showed this same curvilinear association of dilution with increasing flow. The example of manganese is seen in Figure 4.10.

A plot of sulfate versus acidity from the Arnot 004 discharge data showed the expected positive association but again the scatter around a straight line is very large. The expected association of calcium and magnesium is extremely weak. Any relationship between manganese and total iron is obscured by an extreme value in iron. It seems somewhat strange that the data from Arnot 004, which is located between Arnot 001 and 003, should present such a confused picture of these bivariate relationships relative to those of Arnot 001 and 003 data; possibly Arnot 004 contains more outliers than 001 or 003.

Time Series Analysis

A qualitative time series analysis was performed by plotting successive variables against (equal interval) time periods. It is convenient to start with the variable discharge (flow) for Arnot 003 (Figure 4.11a) which may be compared with the same plot on a much larger scale (Figure 4.2). The four maxima (peaks) are quite striking in both graphs. Since the date of the first observation is January 28, 1980, the first peak is in March (1980), marked in the graph by the number 3; the numbers in Figure 4.11a go from 1 to 10 (=0) and then start at 1 again and so on for each cycle of 10. The next peak is 22 (March, 1981) followed closely by another at 26 (May, 1981). Subsequent peaks occur at 43 (March, 1982), 48 (June, 1982) and then 73 (April, May, 1983). Suppose there existed an annual cycle (i.e., 26 observations, one every two weeks) then, starting with March = 3, the next peak should be 29, then 55, 81, etc. Missing observations (see Figure 4.2) and peak discharges at varying intervals, not equal annual cycles, make a seasonal pattern obscure.

Using discharge as the base which controls the concentration of acidity for example, one would expect pH to also show similar cycles in Figure 4.11b. Instead, the first peak and the following double peak are similar to those shown by discharge, but the peak at 40 is not. There is a peak at 48 in both plots but then the pH declines and stays below its mean throughout the subsequent series; there is no sign of the discharge peak at 73. The scatter diagram of pH vs. discharge showed no relationship.

The relationship between acidity and time (Figure 4.11c), tends to be inversely related to the relationship between discharge and time, i.e., the peaks of discharge coincide with the minima (maximum dilution) of acidity. This is supported by the scatter diagram between acidity and discharge (Figure 4.9). There is a slight tendency for this to be true of total iron (Figure 4.11d) but there was no sign of such a relationship in the scatter diagram of iron vs. discharge.

Sulfate, as expected from its scatter plot against discharge shows inverse relationships in Figure 4.11e, with peaks coinciding with discharge troughs. Calcium, magnesium, manganese, and

aluminum also show this inverse relationship to discharge (see Figure 4.11f of aluminum for example).

Figure 4.11a: Plot of Discharge vs. Time (Arnot 003)

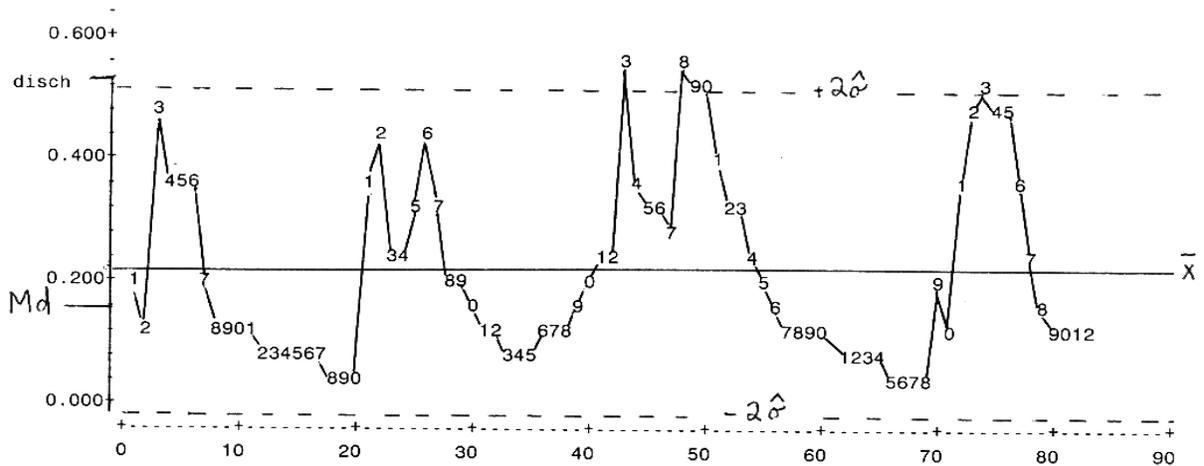


Figure 4.11b: Plot of pH vs. Time (Arnot 003)

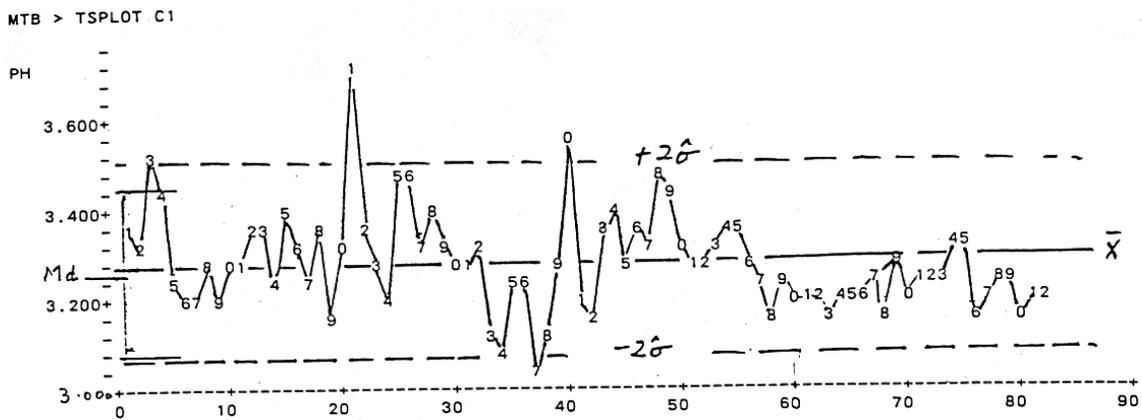


Figure 4.11c: Plot of Acidity vs. Time (Arnot 003)

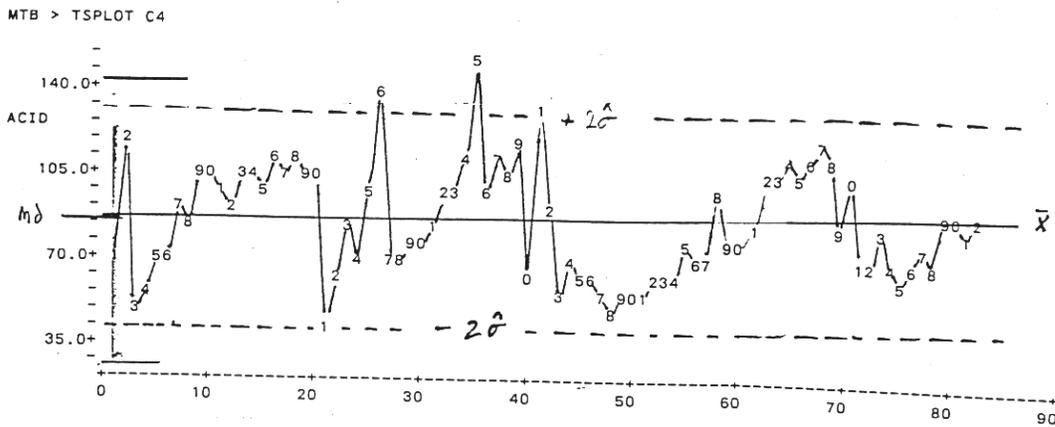


Figure 4.11d: Plot of Total Iron vs. Time (Arnot 003)

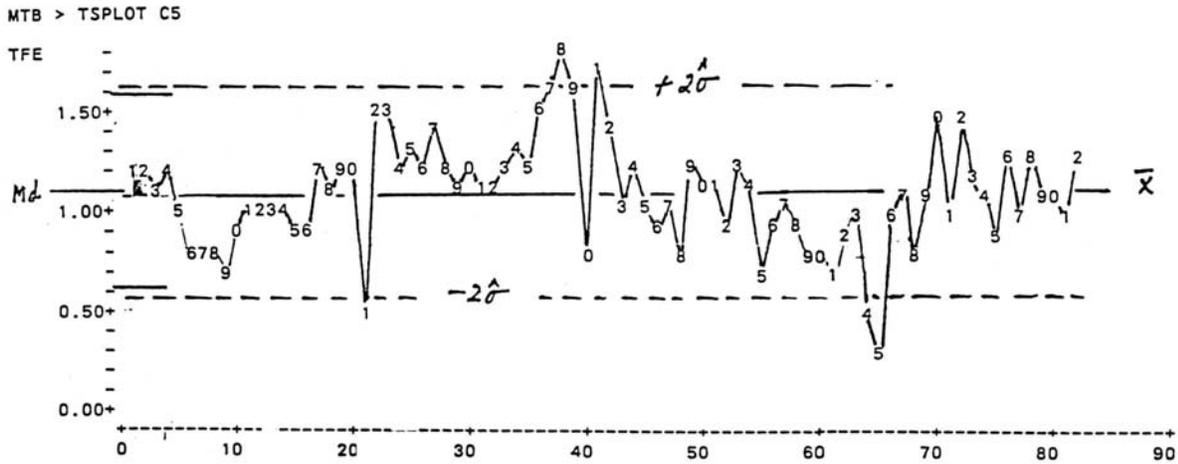


Figure 4.11e: Plot of Sulfate vs. Time (Arnot 003)

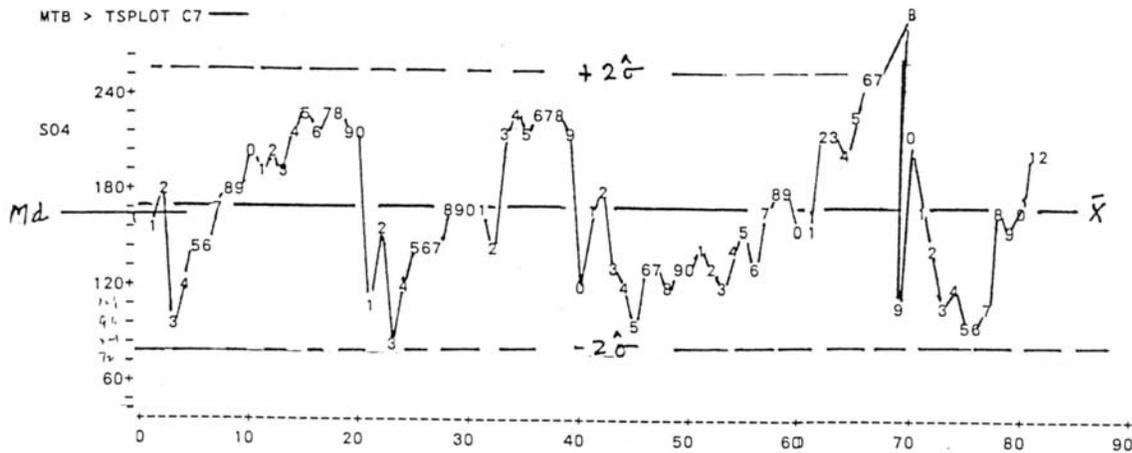
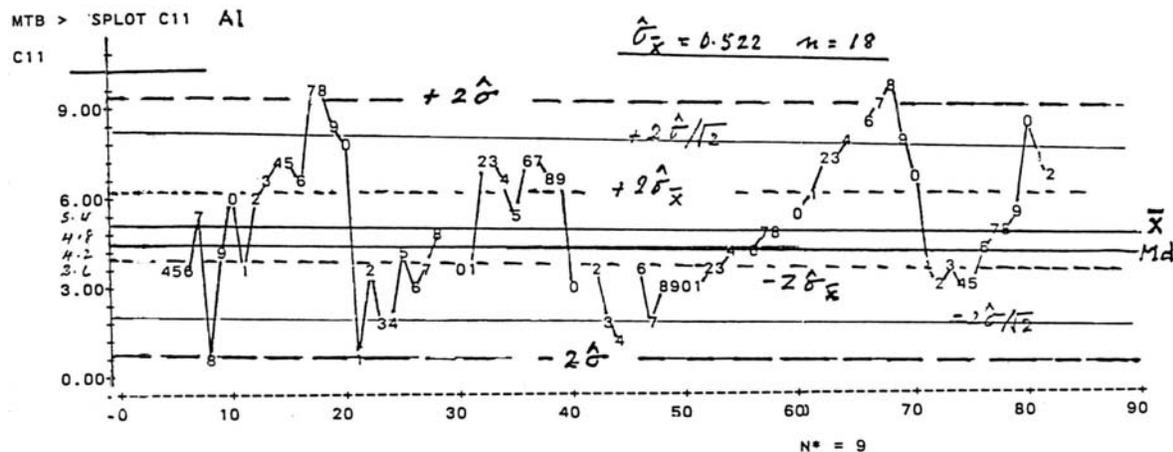


Figure 4.11f: Plot of Aluminum vs. Time (Arnot 003)

The time series plots shown in Figures 4.11a to 4.11f can be used as quality control graphs in the following manner. Confidence limits around the mean are simple to prepare from the descriptive statistics in Tables 4.1a to 4.1c and these can be inserted in, for example, Figure 4.11c. Two kinds of confidence limits are included for comparison. The first is based upon the mean and standard deviation of the normal frequency distribution. The second is based upon the median and other order statistics and is for use in cases where the frequency distribution is not normal (e.g. skewed) or in other non-parametric applications. These two kinds of quality control approaches are discussed in more detail in Chapter 5. The most typical quality control limit is the conventional range of the mean (plus or minus two standard deviations) which, in a normal distribution includes some 95 percent of the observations (i.e., one expects in a moderately long (say > 30) series about 2 – 3 observations outside these limits on either side of the mean). If we wish to relax the requirement of a normal distribution we may use the range encompassed by order statistics, for example $Md \pm 1.58$ (H-spr.), which is approximately equivalent to the conventional measure (Velleman and Hoaglin, 1981, p. 81). The multiplier (2) in the conventional example may be replaced with 3 for a more stringent test in which only 3 in 1000 are expected to fall outside the (3σ) limits, strictly in a normal distribution. The limits for each of the eleven variables from the Arnot 003 data are displayed in Table 4.3, including the range around the means and around the medians. The range around the mean exceeds that around the median in pH, temperature, ferrous iron, and total iron, whereas the range around the median exceeds that around the mean in the seven other variables. These seven variables show associated variation either directly or inversely so this consistency is to be expected. The reason for the reversal in relationship for the other four may arise from inconsistent occurrence of outliers in the data for these variables. pH is usually symmetrical and probably closely normal; temperature, ferric iron and total iron have very marked peculiarities.

Table 4.3: Comparison of Confidence Belts Around Mean and Median (Arnot 003 Data)

	Mean	Std. Dev.	Median	H-spr.	Lower	Upper	Lower	Upper	Range	
Variable	\bar{X}	$\hat{\sigma}$	Md	Q3 - Q1	Around Mean		Around Median		Mean	Median
pH	3.2782	0.1095	3.265	0.1225	3.059	3.497	3.071	3.459	0.438	0.388
Temperature	8.551	0.916	8.6	0.9	6.719	10.383	7.178	10.022	3.664	2.844
Flow	0.2157	0.1509	0.161	0.2272	-0.086	0.518	-0.198	0.52	0.604	0.718
Acidity	86.37	22.55	84.5	36.25	41.27	131.47	27.225	141.775	90.2	114.55
Total Iron	1.0963	0.2843	1.1	0.3	0.528	1.665	0.626	1.574	1.137	0.948
Ferrous Iron	0.361	0.234	0.3	0.2	-0.107	0.829	-0.016	0.616	0.936	0.632
SO ₄	168.99	43.79	165	77.25	81.41	256.57	42.945	287.055	175.16	244.11
Ca	59.75	11.69	61	20	36.37	83.13	29.4	92.6	46.76	63.2
Mg	73.6	23	70	34	27.6	119.6	16.28	123.72	92	107.44
Mn	3.203	1.338	2.76	2.31	0.527	5.879	-0.89	6.41	5.352	7.3
Al	5.079	2.213	4.68	3.56	0.653	9.505	-0.945	10.305	8.852	11.25

The mean, median, and their associated ranges are included in Figures 4.11a to 4.11f. The means and medians are reasonably close with the median usually being less than the mean. This suggests that the outliers are on the large side (i.e., positive skewness) and are pulling the mean up more than the median. The seven variables which show associated variation should probably all be log transformed. The pH is already in log units, but temperature and the iron variables are not, on the whole, consistent enough to make any general recommendation. Total iron or any combination of these should be carefully checked because their variation is open to a variety of problematic explanations, and until one can be sure that these measures are meaningful, they should be treated with circumspection.

From the point of view of setting up triggers, either of the ranges around the mean or median would suffice. If the confidence belts were constructed around the mean, then for the Arnot 003 data, the following observations fall on, near or totally outside them, as shown in Table 4.4. Apparently the 2 sigma limits are more sensitive to these deviations and the H-spread usually shows less observations outside the limits; since 2 sigma = about 95% confidence limits, then 2.5 are expected to exceed the upper limit. Three, therefore, is an expected number and needs no reaction. The iron observations are again somewhat inconsistent.

Table 4.4: Observations Falling Beyond Confidence Limits of 2 Standard Deviations Around the Mean Beyond the (1.58*) H-Spread (Arnot 003 Data)

Variable	Number of Observations	
	>2 $\hat{\sigma}$	>(1.58) H-Spread
pH	4	8
Temperature	3	7
Discharge	3	3
Acid	3	1

Variable	Number of Observations	
	$>2 \hat{\sigma}$	$>(1.58) \text{ H-Spread}$
Total Iron	6	8
Ferrous Iron	2	8
SO₄	1	0
Ca	2	0
Mg	3	2
Mn	5	0
Al	0	0

The approach to Box-Jenkins Time Series analysis may be simplified to accomplish preliminary exploration of the data. We may, therefore, examine the autocorrelation function (Acf) and the partial autocorrelation function (Pacf) to the data and evaluate their first differences, if necessary. From this analysis it can be decided whether the data appear to represent the Integrated Moving Average (IMA) (0,1,1) model described in Chapter 3, or whether a new model should be fitted.

In general, if the Autocorrelation Factor (Acf) looks more or less J-shaped (e.g., Figure 4.12a for Arnot 001 discharge data), it is close enough to the model already described to need no further analysis. If it is subsequently decided to pursue the analysis to model fitting then the full Box-Jenkins procedures described in Chapter 3 should be undertaken.

For the Arnot 001 data, the Acf for discharge (Figure 4.12a), calcium (Figure 4.12b), and aluminum (Figure 4.12c) all conform to the J-shape and are considered to be adequately modeled by an IMA (0,1,1) model. The total iron (Figure 4.12d) and ferrous iron graphs do not show this form of Acf so would require a more formal analysis. From these Acf's, however, it is suspected that a simple Moving Average (MA) (0,0,1) would be adequate to represent these data. In other words, the data appear to represent a random walk.

Figure 4.12a: Autocorrelation Function of Discharge (Arnot 001)

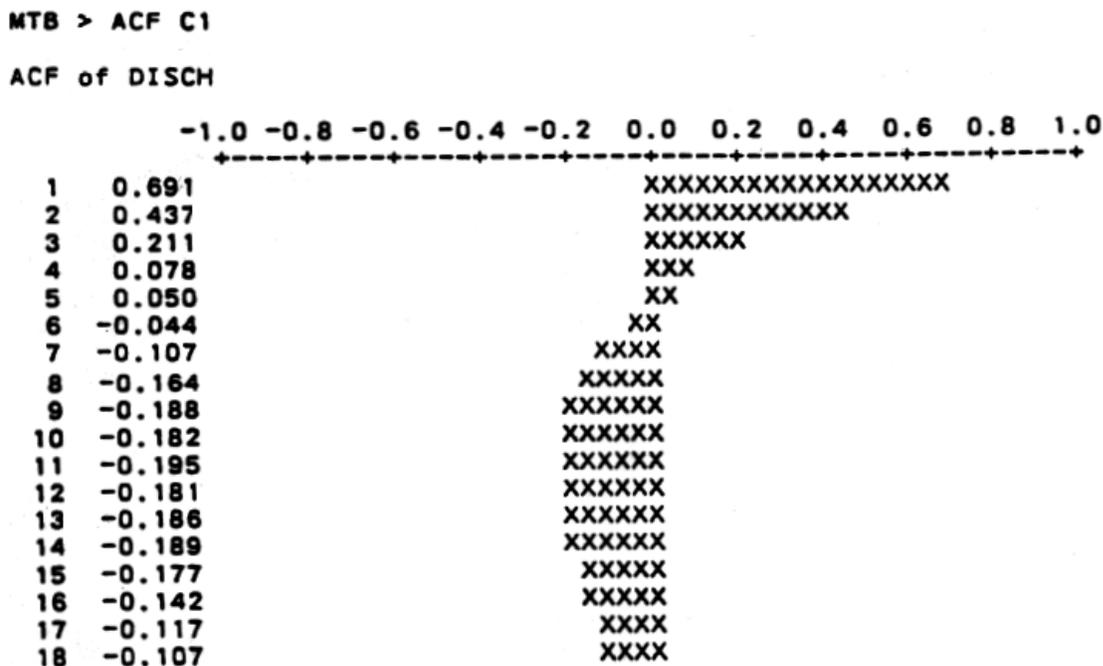


Figure 4.12b: Autocorrelation Function of Calcium (Arnot 001)

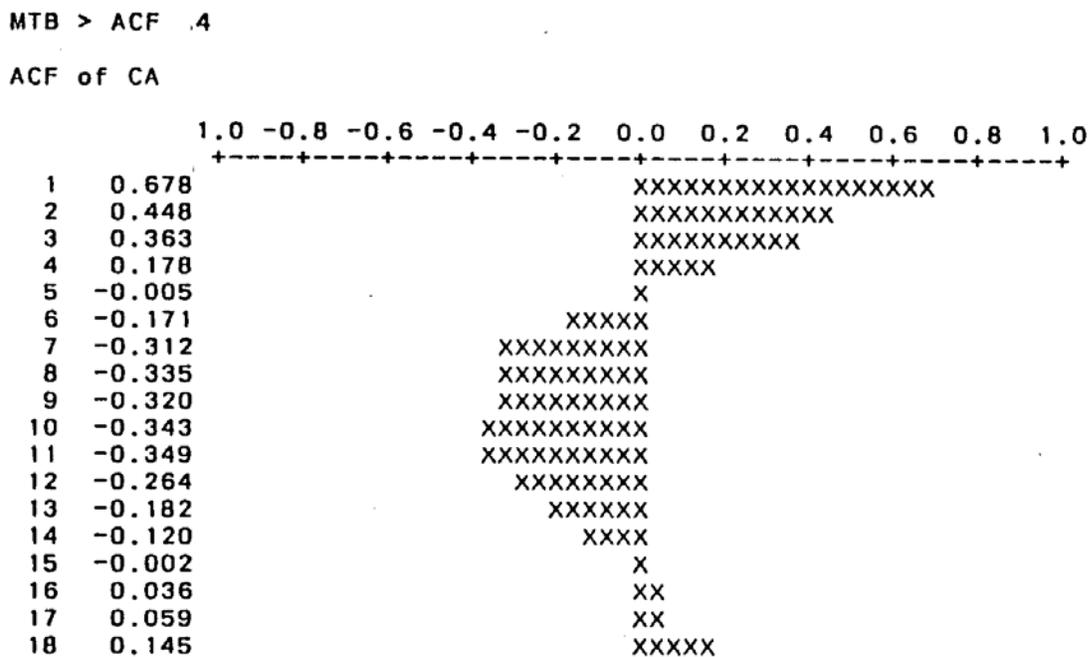


Figure 4.12c: Autocorrelation Function of Aluminum (Arnot 001)

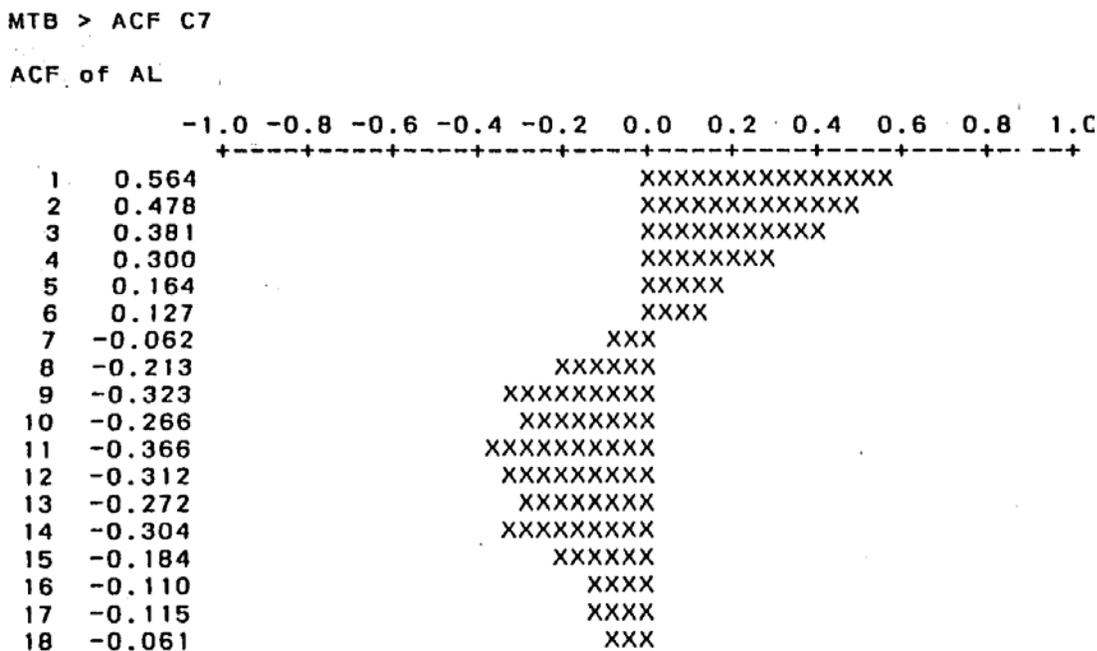
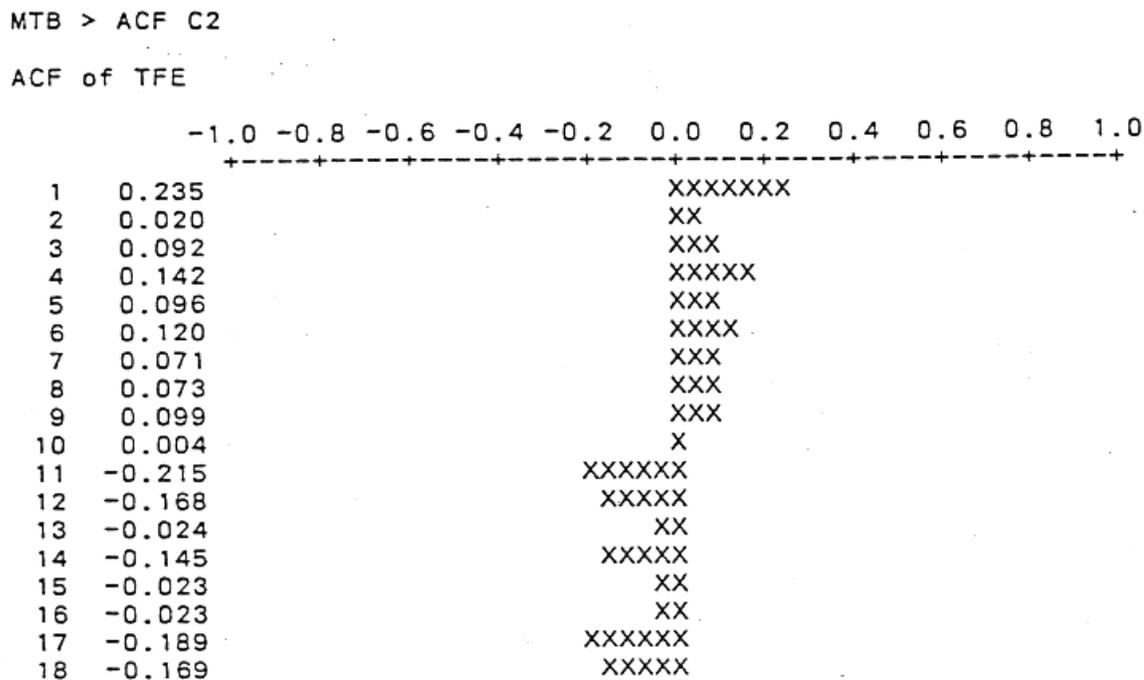


Figure 4.12d: Autocorrelation Function of Total Iron (Arnot 001)



To check these conclusions, the discharge parameter was run through the full Box-Jenkins autocorrelation function analysis and, as in Chapter 3, a first difference was required to reduce the Acf to that expected from white noise. An autoregressive integrated (ARI) (1,1,0) model was fitted for diagnostic purposes, and while most criteria were satisfactory, the confidence belts around the coefficient of the differenced series included zero. For that reason, this model was rejected and the IMA (0,1,1) appears most appropriate. This analysis of Arnot 001 data was then terminated.

Arnot 003 data yielded similar results and the Acf's of discharge and log discharge were almost identical. Acf's for calcium, magnesium, manganese, and aluminum were similar in form; total iron and ferrous iron are peculiar and probably representative of random variation. A comparison of the standard deviations of the raw data from Table 4.1b and the residuals after fitting the model is illustrated in Table 4.5. There is little improvement from fitting the models, further confirming that the variation in these data are essentially random.

Table 4.5: Comparison of Total Iron and Ferrous Iron

Variable	$\hat{\sigma}$	$\hat{\sigma}_e$
Total Iron	0.284	0.252
Ferrous	0.239	0.231

A few examples of the Acf-Pacf analysis are also included for selected variables from the analysis of the Arnot 004 data. The Acf of pH (Figure 4.13a) is not very informative and the Pacf is identical (Figure 4.13b). Without further analysis these data may be taken to represent a random walk. Log discharge in Figure 4.13c possesses typical features of the IMA (0,1,1) model, a rapid decline in the Acf (J-shape) and a single large spike in the Pacf (Figure 4.13d). These features suggest a first difference followed by a first order moving average model.

Figure 4.13a: Autocorrelation Function of pH (Arnot 004)

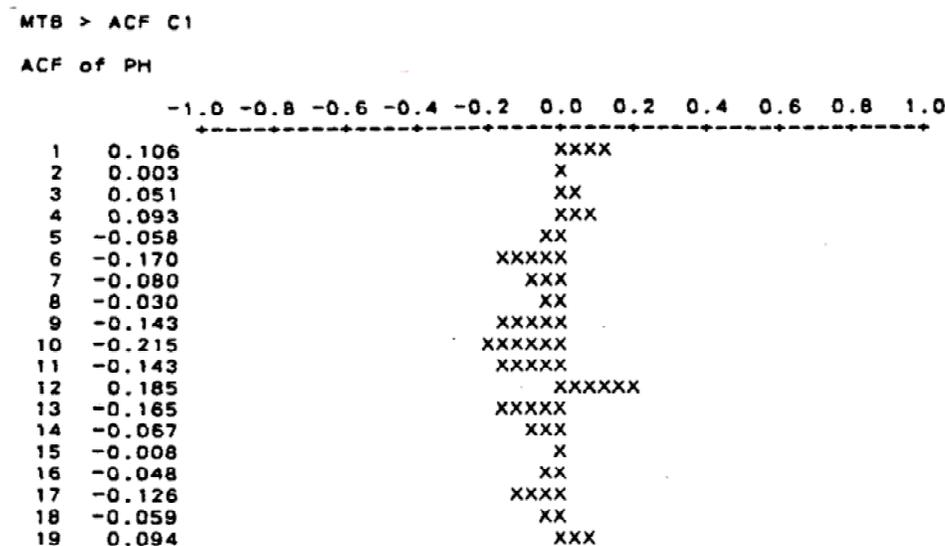


Figure 4.13b: Partial Autocorrelation Function of pH (Arnot 004)

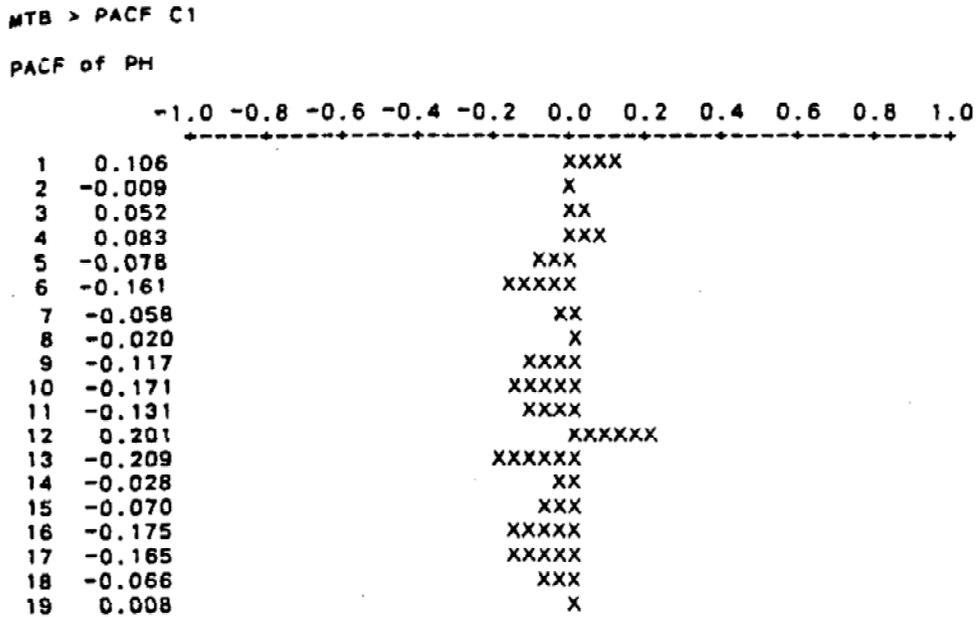


Figure 4.13c: Autocorrelation Function of Log Discharge (Arnot 004)

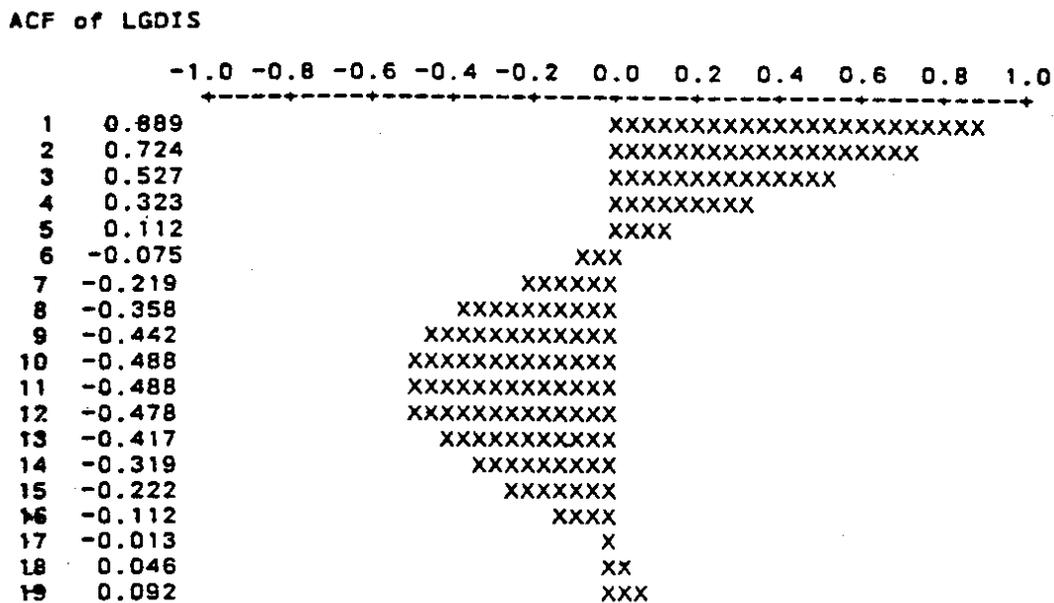


Figure 4.13d: Partial Autocorrelation Function of Log Discharge (Arnot 004)

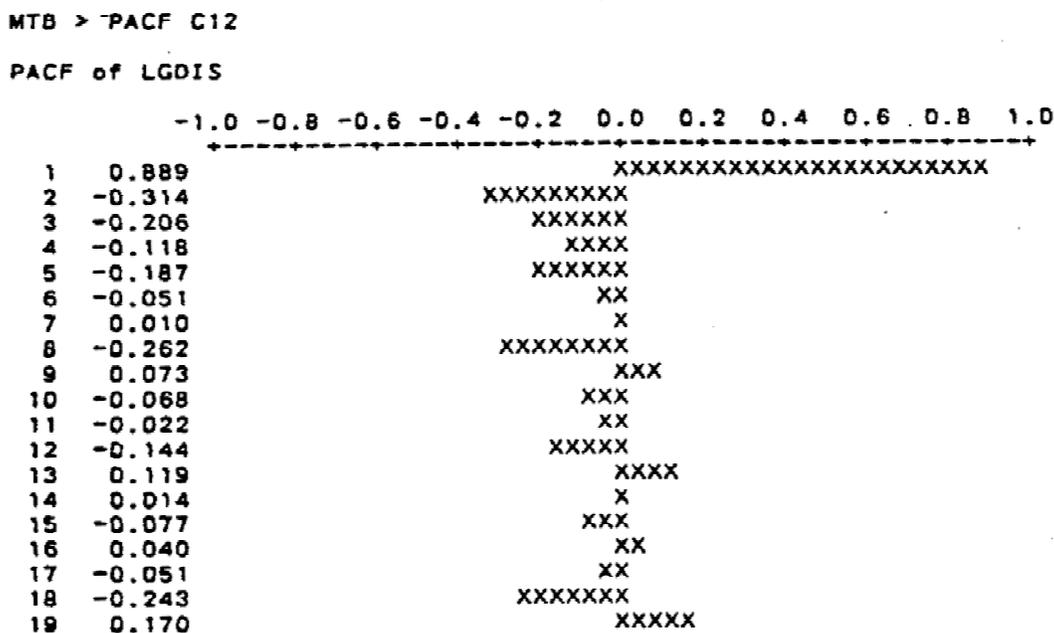


Figure 4.13e: Autocorrelation Function of Ferric Iron (Arnot 004)

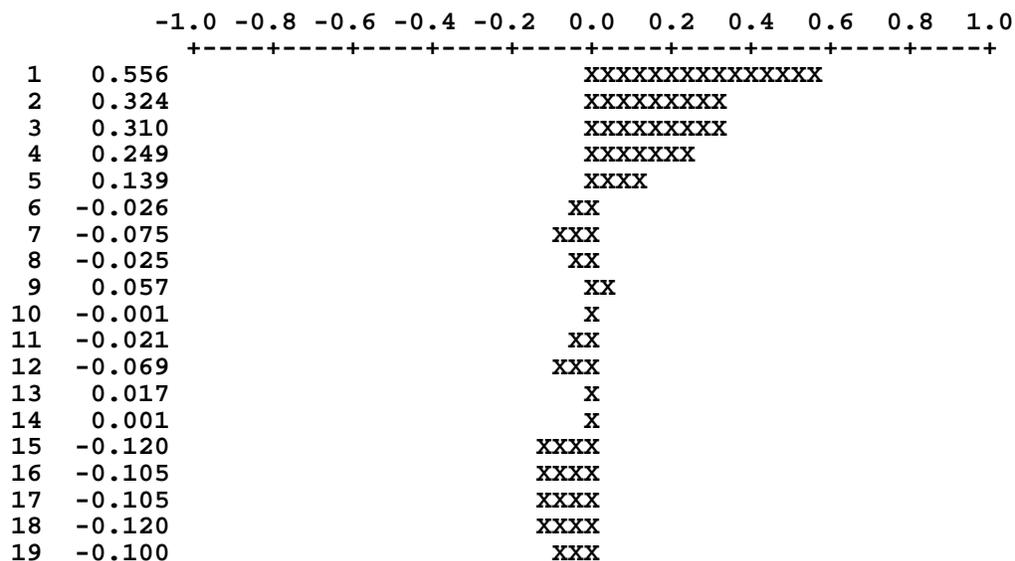
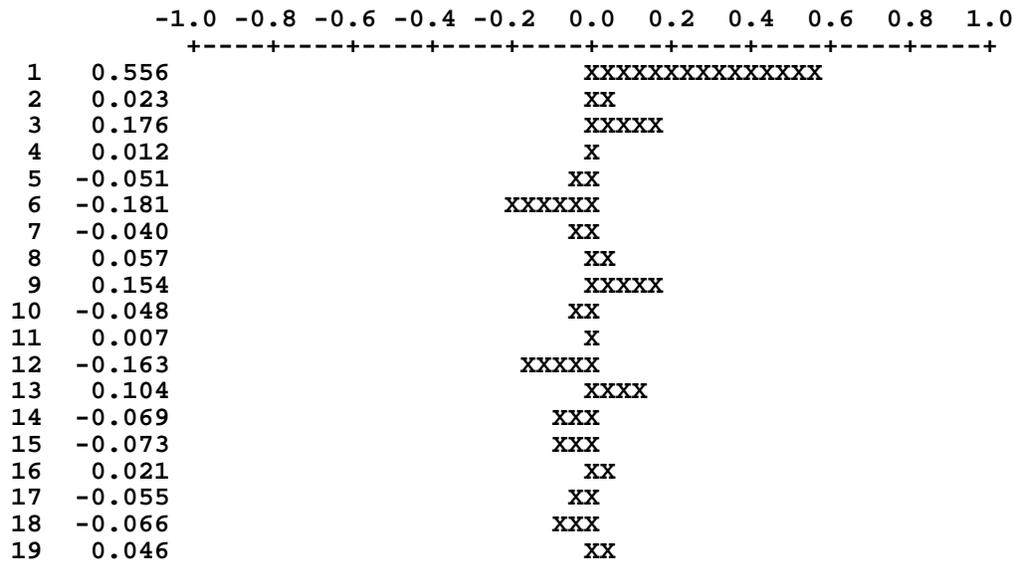


Figure 4.13f: Partial Autocorrelation Function of Ferric Iron (Arnot 004)

Ferric iron shows similar patterns to log discharge, suggesting an IMA (0, 1, 1) model. This is similar to some of the measures of iron content in Arnot 001 and Arnot 003.

Summary

One of the most interesting features in the time series analyses of the Arnot site is the absence or lack of obvious seasonal patterns. Based upon this data set, it appears that this arises for the following reasons:

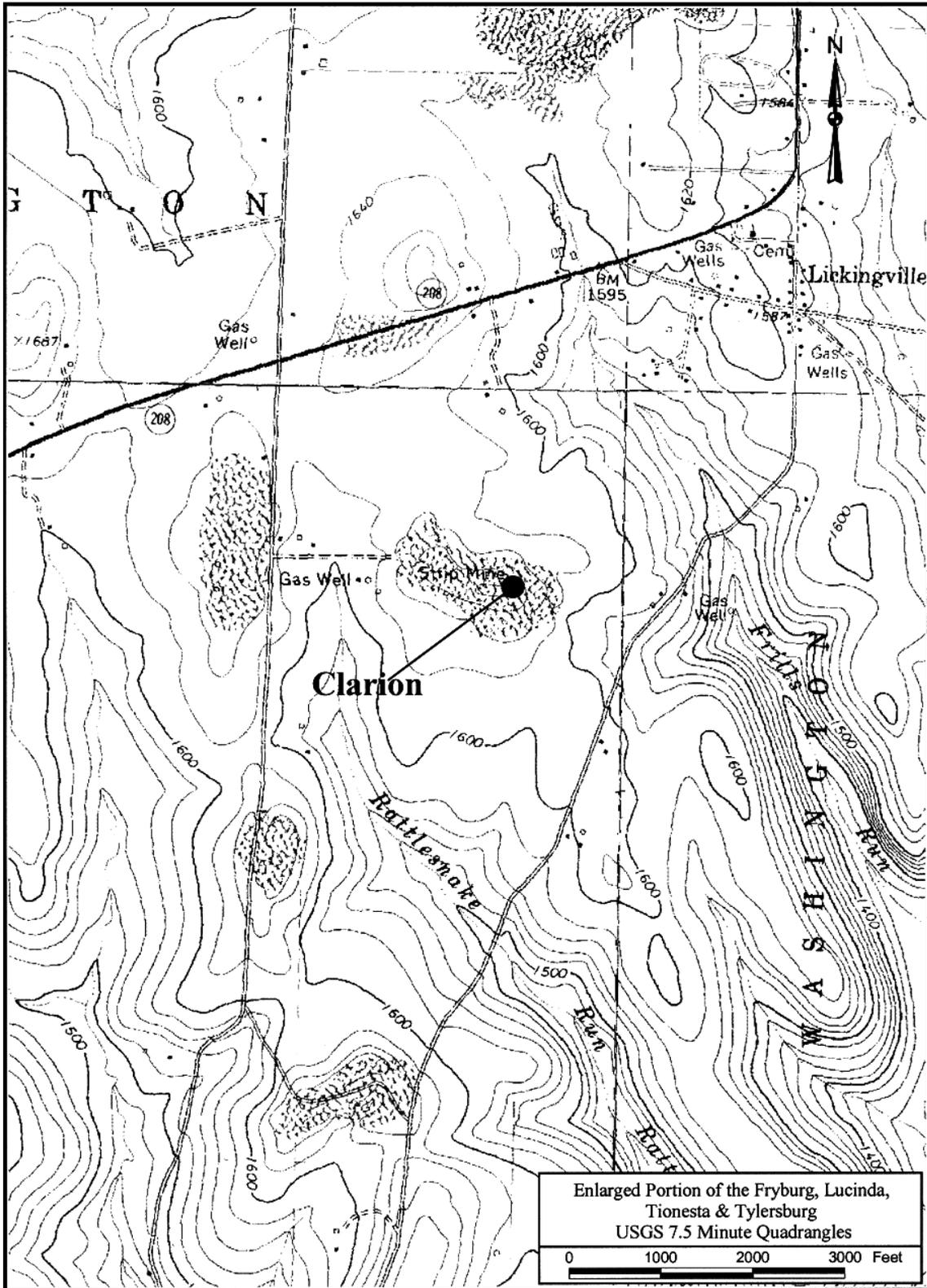
- The peak flow occurs during Spring snow-melt and runoff. This varies over several months, from February to April, so that successive maxima may not occur at the same time each year.
- Another peak flow may occur in early summer as the result of intense short duration storms. Again this is not strictly confined to exactly the same period from year to year.
- If the missing values occur during these events, and they often appear to be so related, then the extreme values do not occur in a uniform cycle; this confuses any seasonal pattern which may be present.

Chapter 5: Analysis of Data from the Clarion Site

The Clarion mine site is located in northern Clarion County, Pennsylvania, in the northwestern portion of the bituminous coal region. The acid mine discharge (S3CLAR) was from an abandoned surface mine on the Upper and Lower Clarion coal seams that was the site of abandoned mine reclamation and a cooperative research project by the Bureau of Abandoned Mine Reclamation of the Pennsylvania Department of Environmental Resources and the U.S. Bureau of Mines. During this project, alkaline addition (in the form of crushed limestone) was incorporated into the reclamation procedures as an attempt to reduce the acid mine drainage pollution, as described by Lusardi and Erickson (1985). A map of the Clarion site is shown in Figure 5.1, which is adapted from Lusardi and Erickson (1985).

The data set used for most of the statistical analysis of the Clarion site contains 96 samples for the time period from December 15, 1981 to August 4, 1986. Of these data, approximately half ($N = 49$) are pre-treatment, and the other half ($N = 47$) are post-treatment with the crushed limestone, alkaline-addition reclamation procedure. Missing data presented a problem in the statistical analysis of the discharge and water quality characteristics.

Figure 5.1: Map of Clarion Mine Site



Univariate Analysis

Initially, there were 104 observations in this data set. However, at least 19 samples were missing flow measurements, and others were missing one or more water quality parameters. Discharge and pH were plotted against date to see where the largest gaps occurred. After careful examination, the data set was reduced to 96 rows containing seven columns: pH, discharge, acidity, total iron, sulfate, ferrous iron, and ferric iron. Ferric iron is determined by subtracting ferrous iron from total iron. The statistics describing the variables were derived and mean values were inserted in rows with missing values. The data were then rerun to yield Table 5.1.

Table 5.1: Summary Statistics for S3CLAR (N=96)

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
pH	96	0	3.696	3.195	3.612	0.985	0.101
Discharge	79	17	12.57	6.70	9.09	22.37	2.52
Acidity	96	0	522.4	483.5	505.6	346.4	35.4
Total Iron	96	0	82.40	75.00	79.31	51.01	5.21
Ferrous Iron	96	0	48.38	37.75	45.97	34.46	3.52
SO ₄	96	0	1528.4	1569.0	1525.9	566.0	57.8
Ferric Iron	96	0	34.02	23.60	31.44	32.05	3.3

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	2.670	6.430	3.002	4.455	26.6
Discharge	0.05	172.00	3.60	12.48	178.0
Acidity	1.0	1546.0	232.5	737.7	66.3
Total Iron	8.70	257.00	39.70	110.25	61.9
Ferrous Iron	0.90	143.00	23.87	66.65	71.2
SO ₄	296.0	3241.0	1181.5	1878.2	37.0
Ferric Iron	- 4	152.00	6.00	55.00	94.2

The very high magnitude of variation in discharge is shown by the value of the Coefficient of Variation ($CV\% = \text{standard deviation}/\text{mean} * 100$) = 180.1%. The coefficients of variation for pH and sulfate are reasonable. However, the CV% for acidity and all iron parameters are rather large. Correction for some exceptional values is proposed when the variables take values which are either very unlikely or even sometimes impossible.

The frequency distribution for sulfate appears to be symmetrical (Figure 5.2). However, some variables exhibit positive skewness including discharge (Figure 5.3a) and acidity (Figure 5.4a). Attempts were made to make these frequency distributions more symmetrical by transforming to logarithms, but this transformation over-corrected and resulted in negative skewness.

For example, log discharge (Figure 5.3b) is slightly negatively skewed and log acidity is extremely skewed (Figure 5.4b). It was decided, therefore, to use the data without transformation.

Figure 5.2: Stem-and-leaf of Sulfate

N = 96		
Leaf Unit = 100		
4	0	2333
6	0	45
10	0	677
17	0	8889999
26	1	000011111
38	1	222223333333
(12)	1	444445555555
46	1	6666666667777777
29	1	8888889999
19	2	000011111
10	2	22223
5	2	44
3	2	6
2	2	8
1	3	
1	3	2

Figure 5.3a: Stem-and-leaf of Discharge

N = 77		
Leaf Unit = 1.0		N* = 19
(53)	0	00000000001111222333333344444555555556666667788999999
24	1	00222244444
13	2	001288
7	3	066
4	4	0
3	5	0
2	6	
2	7	
2	8	3
1	9	
1	10	
1	11	
1	12	
1	13	
1	14	
1	15	
1	16	
1	17	2

Figure 5.3b: Stem-and-Leaf of Log Discharge

N = 75		
Leaf Unit = 0.10		N* = 22
4	-1	3000
7	-0	766
11	-0	4330
19	0	01124444
(35)	0	5555566666777777777888889999999
21	1	000111111333344
6	1	55679
1	2	2

Due to the 19 missing discharge values, a second modified data set was prepared by omitting each row with a missing value for discharge; this left 79 rows with complete observations. This step was essential to the study of the association between discharge and other parameters using plotting routines or cross-correlation. Summary statistics for the modified data set are presented in Table 5.2.

Table 5.2: Summary Statistics for S3CLAR Adjusted Data Deck (N=79)

	N	Mean	Median	Trimmed mean	Standard Deviation	Standard Error of the Mean
pH	79	3.624	3.160	3.533	0.967	0.109
Discharge	79	12.57	6.70	9.09	22.37	2.52
Acidity	79	556.1	499.0	542.1	361.2	40.6
Total Iron	79	86.70	78.50	83.80	53.45	6.01
Ferrous Iron	79	51.23	40.00	49.01	35.92	4.04
SO ₄	79	1586.3	1619.0	1578.6	559.6	63.0
Ferric Iron	79	35.47	26.00	32.89	33.80	3.80

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
pH	2.670	6.430	2.950	4.050	26.7
Discharge	0.05	172.00	3.60	12.48	178.0
Acidity	1.0	1546.0	234.0	819.0	65.0
Total Iron	8.70	257.00	43.00	118.00	61.6
Ferrous Iron	0.90	143.00	25.50	73.50	70.1
SO ₄	364.0	3241.0	1193.0	1948.0	35.3
Ferric Iron	-4.00	152.00	6.00	55.20	95.3

In this adjusted data set (N=79), the coefficients of variation for pH, discharge, acidity, total iron, and sulfate remain close to the same values even after adjustment. CV% for ferrous iron and ferric iron were greatly reduced. The frequency distributions showed similar positive skewness except for sulfate which appeared essentially symmetrical.

Bivariate Analysis

In order to have a measure of the degree of linear association among pairs of variables and to ensure that any relationship is not obscured by time lags, cross-correlation functions for each parameter were obtained (Figure 5.5 for N=79 observations). Discharge and pH showed their maximum degree of association at zero lag (0.357, Figure 5.5a) and it is suspected that the value of this relationship is inflated by the one exceptional value. In other words, it is doubtful that these data could be used to substantiate any real degree of association. The maximum degree of association between acidity and discharge is -0.3 (Figure 5.5b); the direction of association (increase of acidity with decrease of discharge) is likely to be correct, but the degree ($r^2 = 9\%$) is

very small. Similarly, sulfate and discharge show several values of cross-correlation greater than 0.2 at lags of 0, 7, 8, and -15, so that no real association can be claimed (Figure 5.5c).

The use of the cross-correlation function in bivariate and time series analyses is discussed in Chapters 3 through 9 of this report. In these chapters, an r value of 0.2 or a more conservative value of 0.3 have been arbitrarily selected as critical values, with the inference that r values of less than these critical values are not significantly different than 0, and therefore can be deleted from consideration. These arbitrary critical values were selected by rounding off the values of r that are significant at the 5% level for the sample sizes contained in this report (e.g., for this data set of the Clarion discharge where $N = 96$, the value of r that is significant at the 5% level with 90 degrees of freedom is 0.205 (Table 22 in Arkin and Colton, 1963, p.155)).

Figure 5.5a: Cross Correlation Function for pH and Discharge

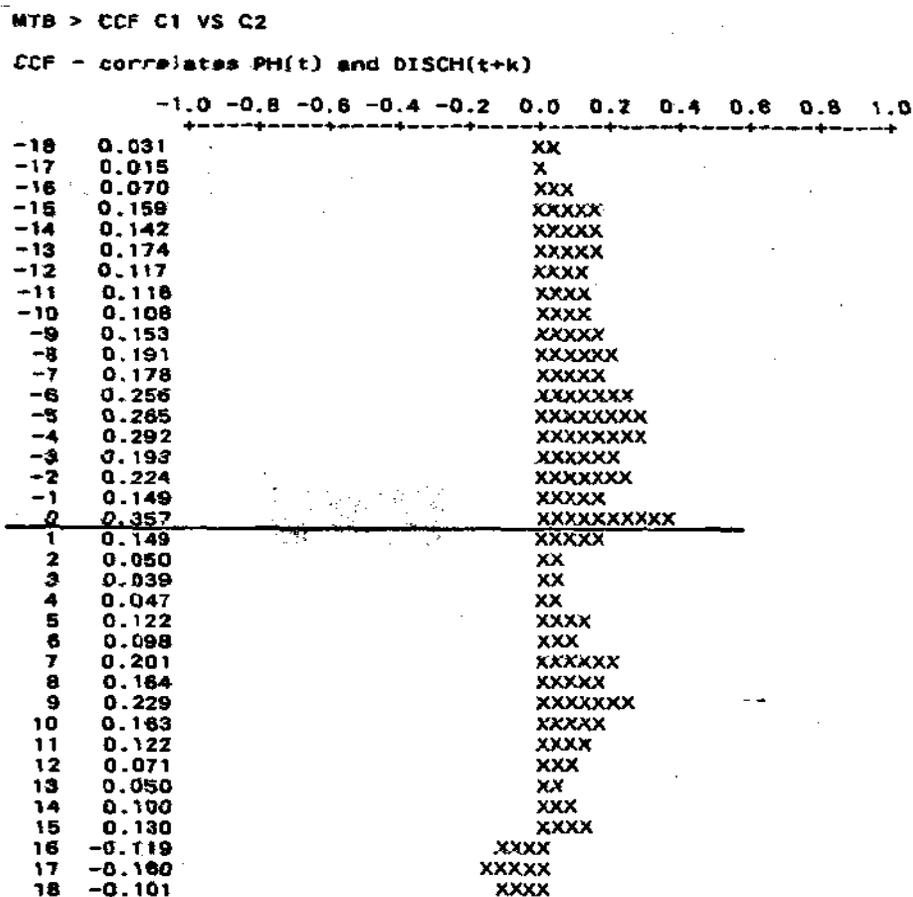


Figure 5.5b: Cross Correlation Function for Acidity and Discharge

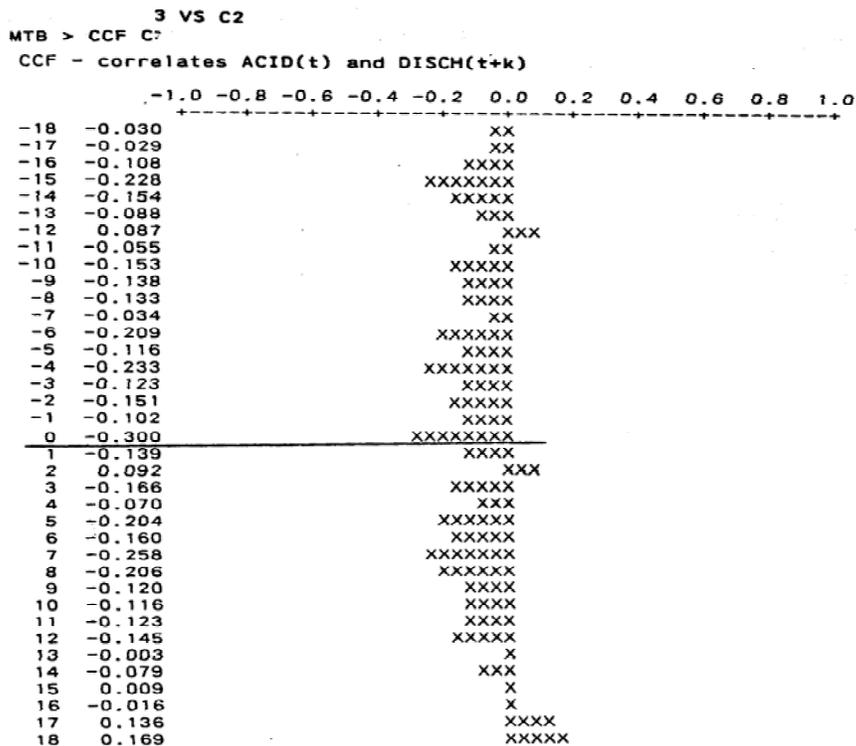
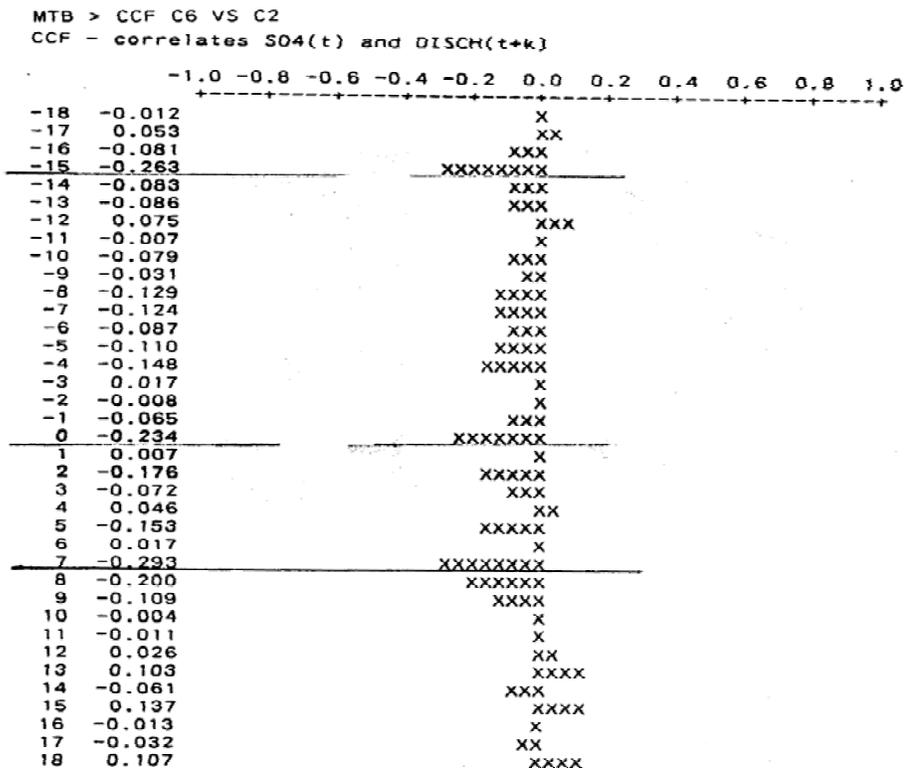


Figure 5.5c: Cross Correlation Function for Sulfate and Discharge



By omitting discharge, it is possible to use the data deck of N=96 and again examine relationships among pairs of variables (see Figure 5.6). The plot of pH against acidity (Figure 5.6a) is curvilinear with pH decreasing rapidly as acidity increases. Below a pH of 3, acidity still increases but the pH stabilizes. Acidity and sulfate (Figure 5.6b) show positive direct linear association with a wide scatter of data points.

Figure 5.6a: Plot of pH vs. Acidity

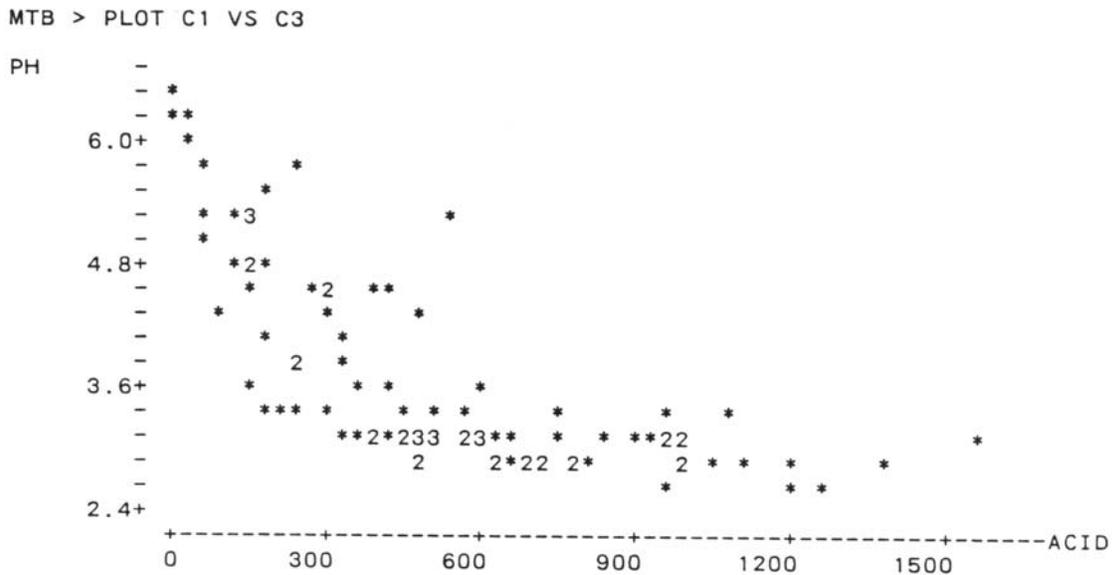


Figure 5.6b: Plot of Acidity vs. Sulfate

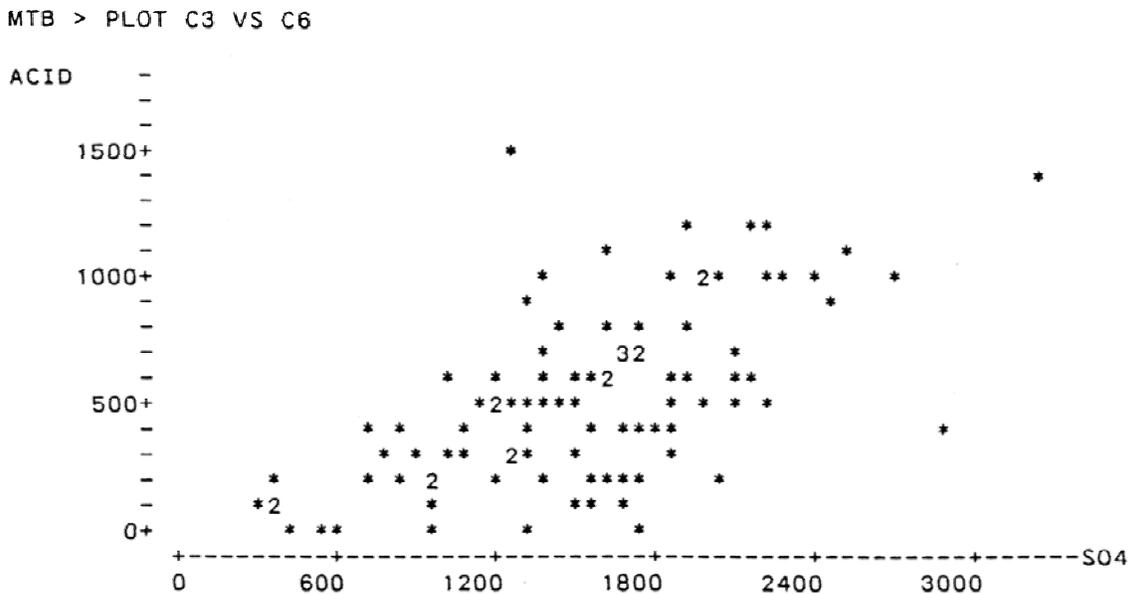
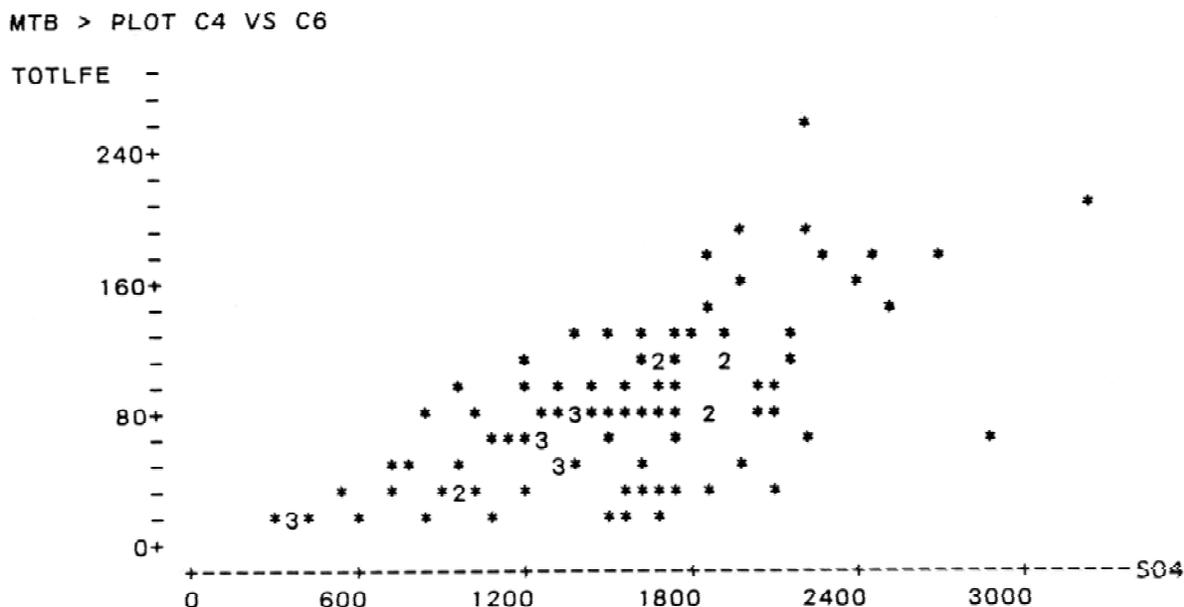


Figure 5.6c: Plot of Iron vs. Sulfate



The importance of these plots is that, despite a wide scatter and tendency to show heteroscedasticity (See Figure 5.6c, total iron vs. sulfate), the association is similar for all pairs of variables (i.e., direct linear association). The comparison of the characteristics of homoscedasticity and heteroscedasticity in bivariate plots of data is described in Chapters 3, 6 and 9 of this report and shown in Figures 6.5a through 6.5c. When the variation of two variables increases as their values increase, heteroscedasticity is present, and it is generally advisable to logarithmically transform these variables, which tends to make the plot of the variables homoscedastic if the standard deviation increases approximately proportionally to concentration prior to transformation.

The persistence of these linear relationships allow us to use one, or at most two, variables for detailed analysis. The conclusions from this analysis may be applied to the other variables. In most cases, there appear to be relationships that are roughly linear. However, the very wide scatter of the data makes the associations rather weak.

Time Series Analysis

Under time series analysis, the data are analyzed in three steps. First, the data may be displayed as graphical plots against time, and quality control limits of two standard deviations (using results from Tables 5.1 and 5.2) may be inserted to show the unusual departures from the mean or median. Second, the data for each variable may be submitted to autocorrelation function analysis (Acf). This permits comparison of variability over time for each parameter and serves to yield a preliminary identification of suitable models for more complex analysis. Third and finally, the data for selected variables are subjected to more complete Box-Jenkins analysis to identify and compare appropriate time series models.

The plot of pH versus time is shown in Figure 5.7a. The most striking feature is the large change in the magnitude of variation after the 50th observation. It appears as if an entirely different environment occurred after the 51st observation (June 30, 1984). Because the two parts of the curve are so different, the two standard deviation limits for the mean underestimate the variation in the later part of the curve. This leads to six values exceeding the two standard deviation limits. It would require data representing a much longer period to determine if this change is a unique circumstance or a regular occurrence.

Figure 5.7b displays a plot of acidity versus time and shows a somewhat different pattern, hence the low degree of association earlier described. Total iron versus time (Figure 5.7c) has a pattern similar to that of acidity versus time, although there is an extreme peak for acidity at time period 73 and iron has smaller peaks at 77 and 79. Sulfate versus time (Figure 5.7d) varies in the same manner as acidity and total iron.

It seems evident that for pH, acidity, total iron, and sulfate there is a break after the 40th observation (Figures 5.7a through 5.7d) reflecting the effect of lime treatment at that time. In this series of graphs, it can be observed that the effect of lime treatment was not persistent, and instead, disappeared with time.

Figure 5.7a: Plot of pH vs. Time

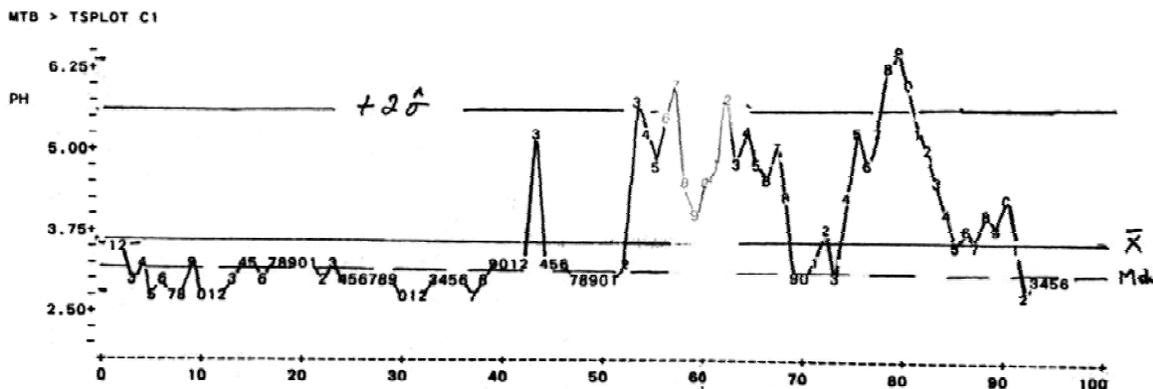


Figure 5.7b: Plot of Acidity vs. Time

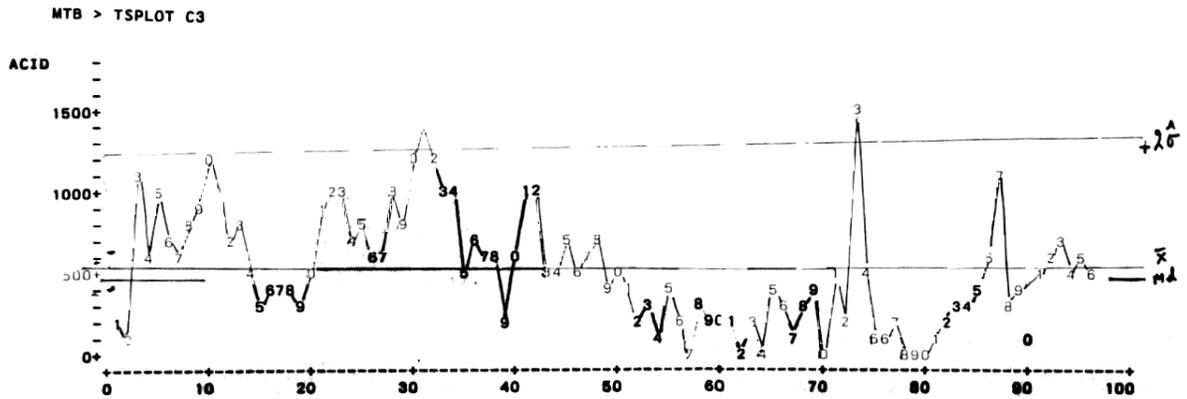


Figure 5.7c: Plot of Iron vs. Time

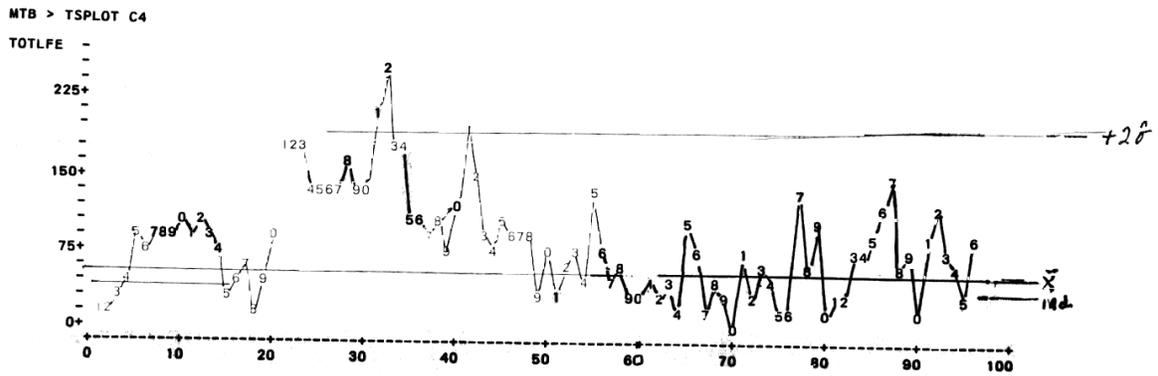
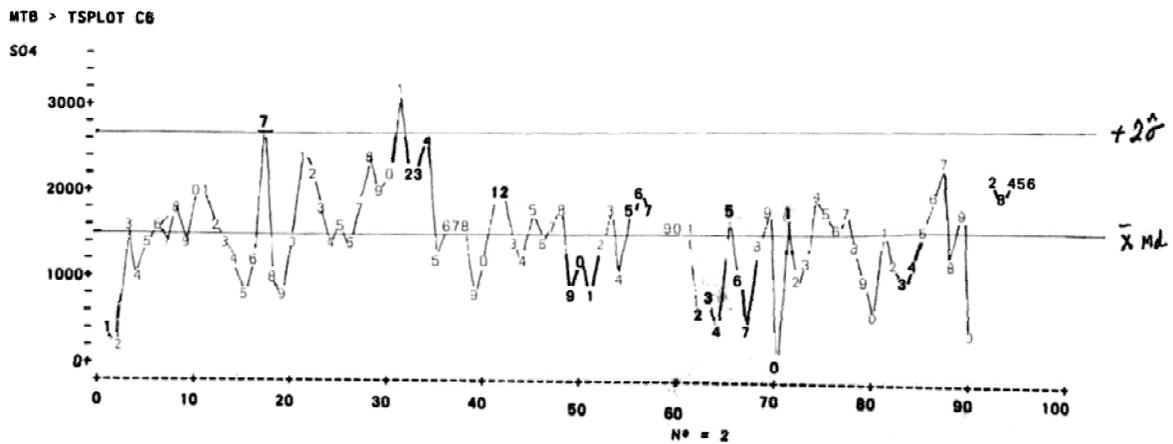


Figure 5.7d: Plot of Sulfate vs. Time



Autocorrelation Functions

It should be noted that the autocorrelation function (Acf) may be used to identify the kind of model which best represents the data for more detailed analysis and curve-fitting. The Acf of pH (Figure 5.8a) shows a sharp decline with increasing lag, and would probably require a first difference to remove this “trend.” Acf’s of acidity (Figure 5.8b) and total iron (Figure 5.8c) are similar and possess similar implications. Sulfate (Figure 5.8d) shows a much weaker degree of autocorrelation but is still of the same general form.

Figure 5.8a: Autocorrelation Function of pH

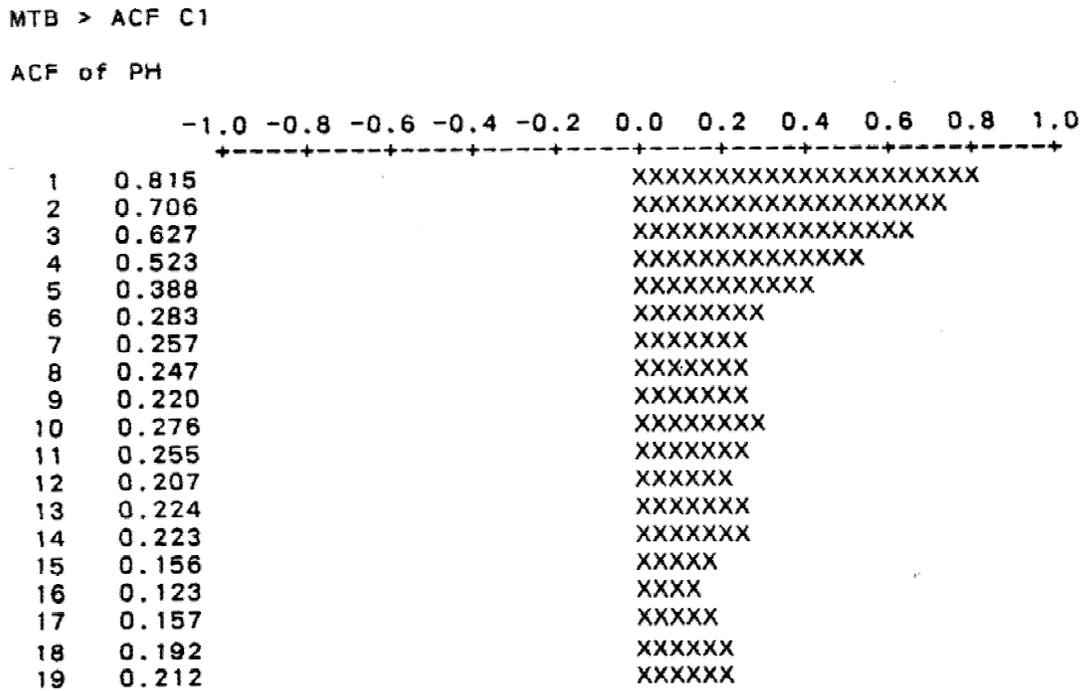


Figure 5.8b: Autocorrelation Function of Acid

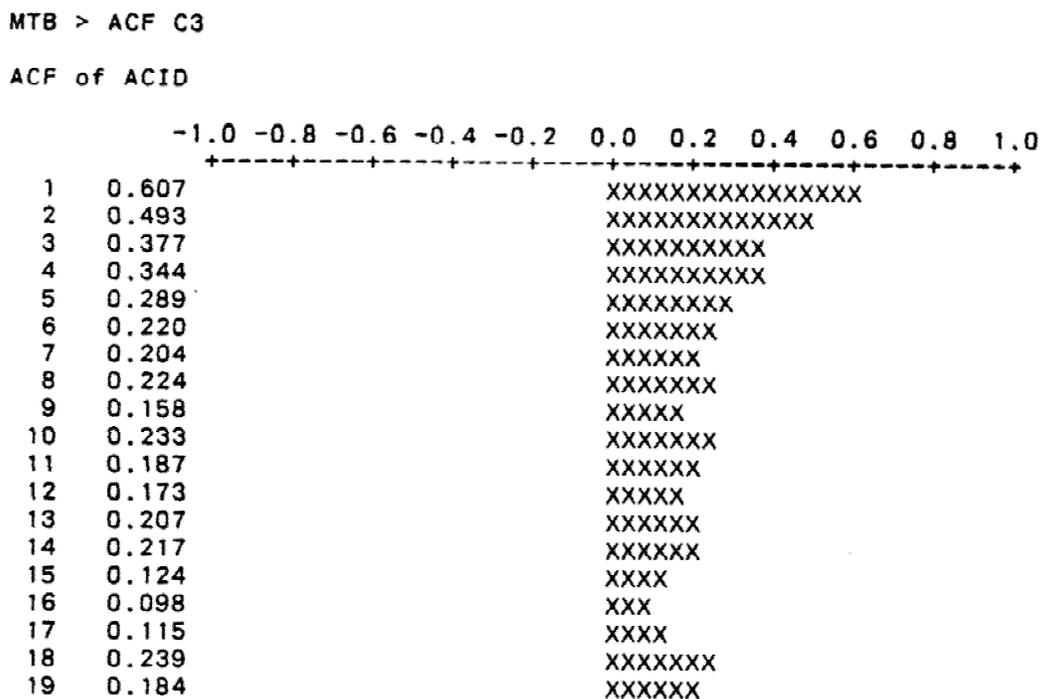


Figure 5.8c: Autocorrelation Function of Total Iron

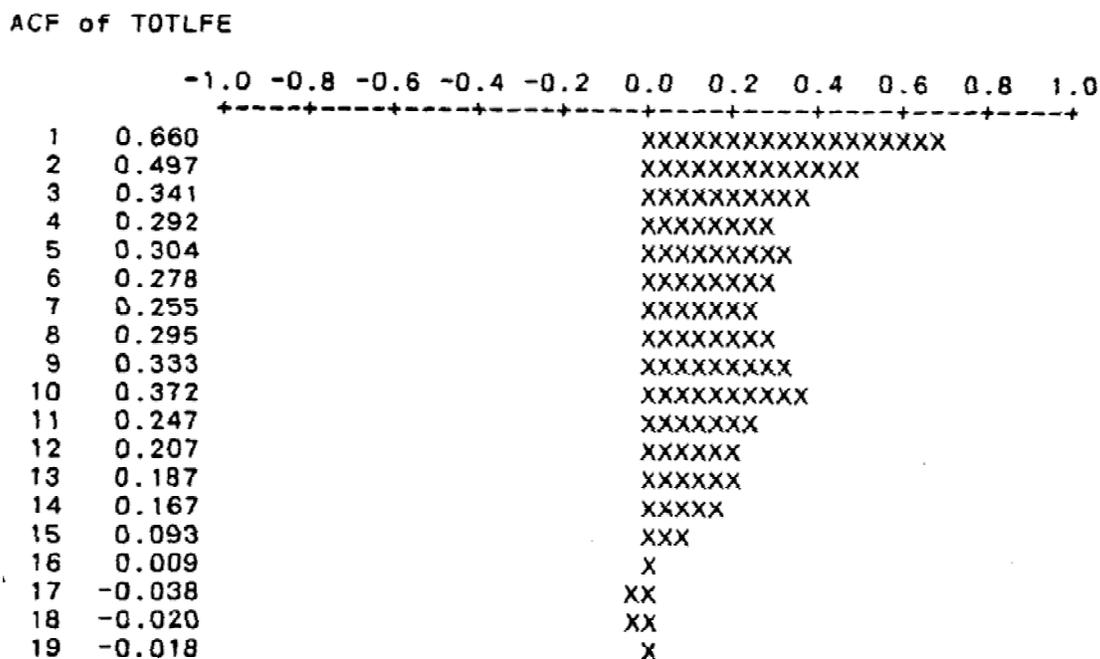
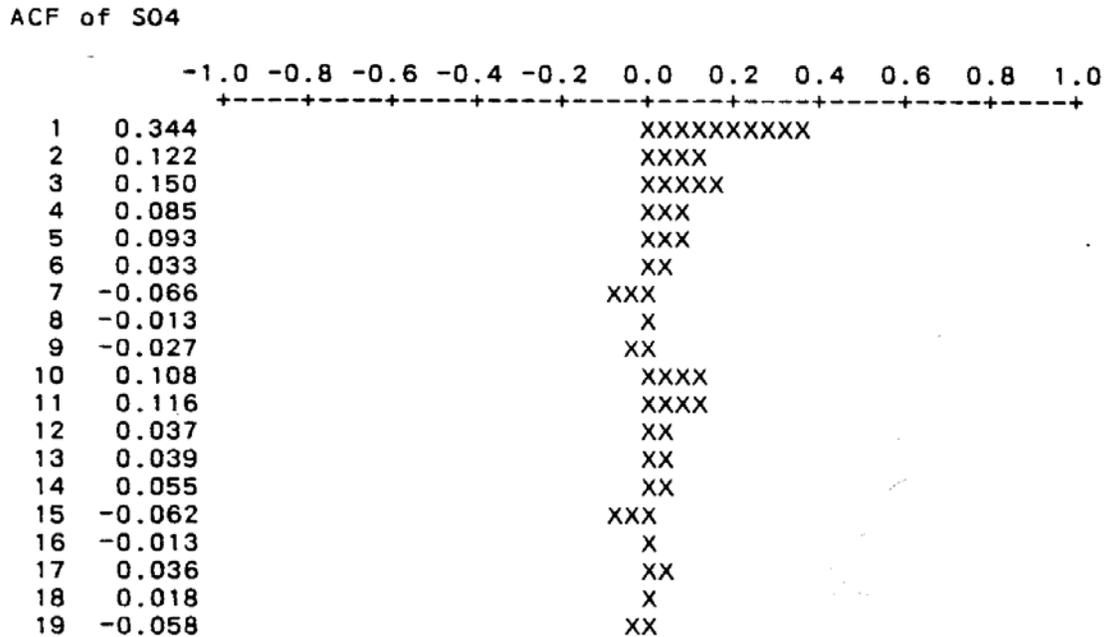


Figure 5.8d: Autocorrelation Function of Sulfate

The ACF of ferrous iron showed no evident pattern and initially, at least, could be considered to show random variation. Ferric iron effectively showed no variation. One cannot but suspect that these variables need careful examination, in regards to field measurement and laboratory testing procedure.

Modeling Selected Variables by Box-Jenkins Time Series Analysis

Three of the variables were chosen for more detailed analysis; pH, sulfate, and ferrous iron. pH shows, essentially, variation that is similar to sulfate. Presumably, they should both possess somewhat similar models. Ferrous iron was included to see if variation was random.

The ACF of first difference for pH gave a chi-square (goodness-of-fit test for the given model) of 40.17 with 25 degrees of freedom yielding a probability of less than 0.05 and greater than 0.02. The original data gave a chi-square of 285.3 with 25 degrees of freedom ($P < 0.001$). Taking a second difference led to an increase in the chi-square value to 70.26 which suggests over-differencing.

The chi-square of 32.56 with 22 degrees of freedom (df) for ACF of residuals after fitting a one step autoregressive AR (1,0,0) model gives a $0.10 > P > 0.05$ (Table 5.3). This effectively reduced the ACF, and the accompanying partial autocorrelation functions (Pacf) possessed what appear to be significant spikes at lags 10 and 19. These spikes were ignored because, to

conclude that they were reflections of real seasonal effects would require the existence of a significant spike at low lags (say at lag 5) and this did not occur. Up to period 42, the residuals are very small. At period 42, there is a serious departure and residuals show larger fluctuations from period 50 onwards.

Table 5.3: Summary of Time Series Models for pH, Clarion Mine

No	Model	Residuals			Standard Deviation	
		Chi-sq.	df	P	Residual	Original
1.	AR(1,0,0)	32.56	22	0.10 > P > 0.05	0.572	0.985
2.	MA(0,1,1)	36.26	23	0.5 > P > 0.2	0.579	0.985

The standard deviations, after fitting either model, are almost the same (Table 5.3) each representing about a 60% reduction. The relevant equations for the models of the pH variable are:

1. AR: $z_t = 0.821z_{t-1} + 3.676 + a_t$
2. MA: $z_t = a_t - 0.247a_{t-1}$

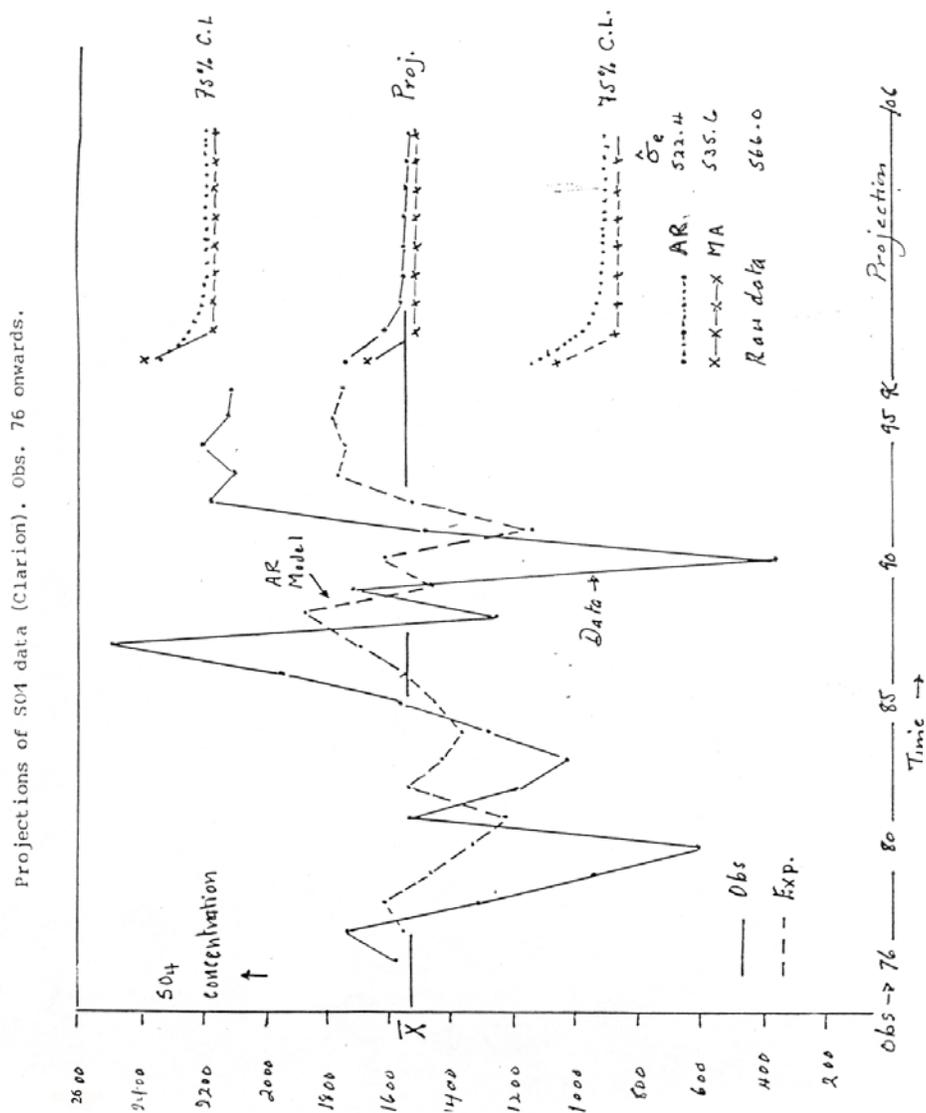
As may be seen in Table 5.4, the two models used for sulfate variation are the AR (1,0,0) and the moving average, MA (0,0,1) models. The chi-square statistics are similar but the AR (1) yields an Acf of residuals without any significant spikes. The MA (1) does not achieve as clean an Acf of residuals.

The standard deviations of the residuals (Table 5.4) from both models offer only minor reduction in the original standard deviation of the raw data (< 10%). A comparison of both models as predictors of future observations is displayed in Figure 5.9. The projections and the 75% confidence limits are similar in both models. It is quite clear that both models show the one step memory and then approximate the overall mean value for the next nine periods. It is fairly evident in Figure 5.9, that the expected values from the AR (1) model fluctuate around the overall mean and fail to duplicate closely, the wide swings present in the raw data. This is because the model is based on the entire record of 96 observations and the fluctuations are very large during the first 35 and the last 30 periods (see Figure 5.7d).

Table 5.4: Summary Statistics for Time Series Models of SO₄ from Clarion Site

N	Model	Residuals			Standard Deviation	
		Chi-sq.	df	P	Residual	Original
1.	AR(1,0,0)	9.184	22	> 0.99	522.3	566.0
2.	MA(0,0,1)	9.204	22	> 0.99	535.6	566.0

Figure 5.9: Projections of Sulfate Data



The relevant equations for the models of the sulfate variable are:

1. AR (1): $z_t = 0.348z_{t-1} + 1550.9 + a_t$
2. MA (1): $z_t = a_t + 0.345a_{t-1} + 1526.1$

Four models were used in an attempt to find a “best” fit for the ferrous iron variable. The usual one step models AR (1) and MA (1) led to satisfactory results which were very similar (Table 5.5). The autocorrelation functions of the residuals from both led to chi-squares of 20.50 and 26.10 respectively. The degrees of freedom were 23 in both cases, and the probability statements are similar. Hence, in effect, either of these models are adequate representations of the raw data. The standard deviations of the residuals were close (29.81 and 31.00 respectively). However, these standard deviations represent very little improvement over the standard deviation of the raw data (see Table 5.5).

Since there were some irregular spikes in the lag 2 position of the autocorrelation functions of the residuals from the first two models, more complex models were applied, (MA (2) and an ARMA(1,1)). From Table 5.5, it can be seen that the outcomes, in terms of probability of achieving a chi-square value as large as these from a white noise (i.e., random) series, is very likely. The standard deviations are close to those of the simpler models and nothing was gained by attempting to fit these more elaborate models.

Table 5.5: Summary of Time Series Models for Ferrous Iron, Clarion Site

No.	Model	Residuals			Standard deviation	
		Chi-sq.	df	P	Residual	Original
1.	AR(1,0,0)	20.50	23	0.6 < P < 0.7	29.81	34.46
2.	MA(0,0,1)	25.10	23	0.3 < P < 0.4	31.00	34.46
3.	MA(0,0,2)	17.60	22	0.7 < P < 0.8	29.76	34.46
4.	ARMA(1,0,1)	20.60	22	0.5 < P < 0.6	29.96	34.46

The relevant equations for the models of the ferrous iron parameter are:

1. AR (1): $z_t = 0.512z_{t-1} + 48.2 + a_t$
2. MA (1): $z_t = a_t + 0.411a_{t-1} + 48.4$
3. MA (2): $z_t = 48.34 + a_t + 0.466a_{t-1} + 0.302a_{t-2}$
4. ARMA (1,1): $z_t = 48.18 + 0.545z_{t-1} + a_t - 0.044a_{t-1}$

Significance tests of the coefficients for ferrous iron suggest they are likely to be real except for the coefficient of the moving average (MA) term in the ARMA model. Because the confidence limits include zero, this model is rejected.

Quality Control Limits

There is a very large number of methods for defining quality control limits and there are arguments for and against all of them. This section of the chapter is an attempt to compare different limits for the Clarion site data. Unfortunately, the standard deviations and spreads for the variables in this data set are very large, and may be atypical. Also, the probability statements refer to comparisons of single samples; multiple comparisons using several samples may require inflation of the control limits or a reduction in the probability statements.

Table 5.6 contains the statistics from which the quality control limits may be derived. The original summary statistics for this data set ($N=79$) are shown in Table 5.2, and Appendix C contains a table of various spreads for this data set. The column in Table 5.6 labeled H-spr/1.349 is included because it is supposed to be an approximate estimate of the standard deviation (Velleman and Hoaglin, 1981, p.54). These values may be compared with the corresponding standard deviations in the adjacent column. The H-spread estimate for the standard deviation of pH is smaller than the observed value. The estimate for the standard deviation of discharge is much smaller than (one-third of) the observed value, probably reflecting the marked skewness of these data, which arises from a few extremely large values. The H-spread estimate for acidity is larger than the observed value, and is suspected to be a reflection of the skewed data. The estimates for sulfate, total iron, ferrous iron and ferric iron are all similar to their observed values.

Table 5.6: Comparison of Statistics used to calculate the QC limits ($N' = 79$)

Variable	Mean	Median	H-spread	C-spread	Standard Deviation	H-spread/1.349
pH	3.624	3.16	1.06	3.38	0.967	0.786
Discharge	12.57	6.7	8.745	50.44	22.37	6.48
Acid	556.1	499	562.5	1381	361.2	416.98
Total Iron	86.7	78.5	73	181.5	53.45	54.11
Ferrous Iron	51.23	40	47.45	128.2	35.92	35.17
SO ₄	1586.3	1619	716	2125.99	558.6	530.76
Ferric Iron	35.47	26	49.15	99.1	33.8	36.43

A number of possible spreads which could be used to set up quality control limits are listed in Table 5.7. The first example is the conventional spread of the mean plus and minus twice the standard deviation. In a normal frequency distribution this would include about 95 percent of the distribution or, alternately, it is expected that about 5 observations in every 100 would fall outside these limits. The constraint of strict normality may be relaxed considerably so that this is a reasonably general confidence interval. This spread would be used to compare to individual results (i.e., $N' = 1$).

Table 5.7: Comparison of QC Limits (Spreads) around Mean and Median

Variable	Mean \pm 2 Standard Deviation		Mean \pm 2 Standard Deviation / $\sqrt{N'}$		Median \pm 1.58 * H-spread / $\sqrt{N'}$	
	LL	UL	LL	UL	LL	UL
$N' = 79$						
pH	1.69	5.56	3.41	3.84	2.97	3.35
Discharge	-32.2	57.3	7.5	17.6	5.1	8.3
Acid	-166.3	1278.5	474.8	637.4	399.0	599.0
Total Iron	-20.2	193.6	74.7	98.7	65.5	91.5
Ferrous Iron	-20.61	123.07	43.15	59.31	31.57	48.43
SO ₄	469.1	2703.5	1460.6	1712.0	1491.7	1746.3
Ferric Iron	-32.1	103.1	27.9	43.1	17.3	34.7

Variable	Median \pm 1.58 * H-spread / $\sqrt{N'}$		Mean \pm 2 Standard Deviation / $\sqrt{N'}$	
	LL	UL	LL	UL
$N' = 18$				
pH	2.77	3.55	3.17	4.08
Discharge	3.4	10.0	2.0	23.1
Acid	289.5	708.5	385.8	726.4
Total Iron	51.3	105.7	61.5	111.9
Ferrous Iron	22.33	57.67	34.30	68.16
SO ₄	1352.4	1885.6	1323.0	1849.6
Ferric Iron	7.7	44.3	19.5	51.4

If the number of samples is taken into account it must be emphasized that the calculated interval refers to means of sets of samples of size N' ; for example, if the number of observations is chosen as base, then $1/\sqrt{N'}$, in this case, $= 1/\sqrt{79} = 0.113$, or for $2 \hat{\sigma} (1/\sqrt{N'}) = 0.226 \hat{\sigma}$. These limits are much too restricted. Relaxing this requirement, to say an $N' = 18$, gives $0.471 \hat{\sigma}$, and this again refers to means based on sample sizes of 18. This would appear to be too restrictive, because too many observations would fall beyond these limits. Similar features apply to each estimate containing N where $\sqrt{N'} > 1$.

Since the sample size is usually one ($\sqrt{N'} = 1$), the multiplier will be 2 times $\hat{\sigma}$ or some equivalent in non-parametric form. The intervals (quality control limits) listed in Table 5.7 show a comparison of the conventional parametric limits (based upon $2 \hat{\sigma}$), together with non-parametric limits ($1.58 \text{ (H-spread)} / \sqrt{N'}$) where the sample sizes are $N' = 79$ and $N' = 18$.

Three different estimates of quality control limits around the median are given in Table 5.8: the median plus or minus the [C-spread], the median plus or minus 1.58 times the [C-spread] over root N , and the median plus or minus 3 times the H-spread. The conventional limits (means 2

$\hat{\sigma}$) are given for comparison in the last column. The spreads are obtained from the Table in Appendix C.

Table 5.8: Comparison of QC Limits around the Median using Various Forms of Spread

Variable	Median \pm C-spread		Median \pm 1.58* C-spread / $\sqrt{N'}$		Median \pm 3 * H-spread		Mean \pm 2 * Standard Deviation	
	LL	UL	LL	UL	LL	UL	LL	UL
pH	-0.22	6.54	1.38	4.94	-0.02	6.34	1.69	5.56
Discharge	-43.7	57.1	-19.9	33.3	-19.5	32.9	-32.2	57.3
Acid	-882.0	1880.0	-228.3	1226.3	-1188.5	2186.5	-166.3	1278.5
Total Iron	-103.0	260.0	-17.1	174.1	-140.5	297.5	-20.2	193.6
Ferrous Iron	-88.20	168.20	-27.52	107.52	-102.35	182.35	-20.61	123.07
SO ₄	-507.0	3745.0	499.3	2738.7	-529.0	3767.0	469.1	2703.5
Ferric Iron	-73.1	125.1	-26.2	78.2	-121.5	173.5	-32.1	103.1

The median \pm C-spread compares reasonably well with the median \pm 3 * (H-spread) in Table 5.8 except for discharge where the latter is much smaller than the former. The quality control limits around the mean yield smaller spreads than either the 3 * (H-spread) or the C-spread, except for discharge. The value of the mean + 2 $\hat{\sigma}$ compares well with the median + C-spread for discharge.

These comparisons of quality control limits shown in Tables 5.7 and 5.8 are more easily understood if the description is illustrated in graphs. Figure 5.7a is a graph of the pH of the discharge from the Clarion site with the mean and median inserted. It is obvious that the extremely high values after the 50th observation (i.e., after treatment begins), affect the mean much more strongly than the median. The difference between the mean and the median is largely due to the pronounced skewness induced by these few large values.

The C-spread and the 3 * (H-spread) quality control limits in Table 5.8 compare very closely. If these limits are used, only one value falls on or near them. About 7 values fall beyond the 2 sigma limits in Figure 5.7a. The spread of 1.58 * (H-spread / $\sqrt{N'}$) is more constraining than these 2 sigma limits; if it were plotted on Figure 5.7a, 14 observations would fall on or beyond this value of spread.

If adjustment is made for a sample size of $N' = 6$, the limits are much more restrictive and the majority of values after the treatment was initiated fall beyond this limit. The lower quality control limits for pH in Table 5.8 fall outside the limits of this graph, but are of little interest in the present circumstances. For pH, these arguments are mostly illustrative because prior to treatment, the values vary around the median of 3.16, indicating the acidic nature of the discharge. After treatment (after the 50th observation in Figure 5.7a), the pH frequently exceeds 5, but only one value exceeds 6. From the 85th observation onwards, the pH has returned to on or below the median value.

The second graphical example of quality control is the plot of sulfate as shown in Figure 5.7d. In both Figures 5.7a and 5.7d it is assumed that the observations are evenly spaced in time, which is not always true (see Figure 4.2 in Chapter 4). In Figure 5.7d, the mean and median coincide fairly closely, suggesting a symmetrical frequency distribution. It seems obvious that the spread of median $\pm 3 * (H\text{-spread})$ is much too wide (i.e., 3717.0); if it were plotted on Figure 5.7d, no observation would come close to it. The spreads of mean plus or minus two sigma and the median $\pm 1.58 * (H\text{-spread} / \sqrt{N'})$ are very similar and either would be equally effective, although the $2 \hat{\sigma}$ limits plotted on Figure 5.7d appear to be more sensitive.

In conclusion, no simple recommendation on quality control limits can be made on the basis of these observations of the Clarion site, which may or may not be representative. It seems likely that establishment of the form of the frequency distribution, particularly symmetry, appears to be most desirable when setting up the quality control limits. It seems clear in this analysis that the limits are not consistent from variable to variable. If this is true in the analyses of data from different sites, then perhaps different forms of spread with different limits may be necessary for each variable.

Summary

It seems clear from the data that there was a marked change in the environment after the 50th observation (May 8, 1984). This is confirmed by the knowledge that “Limestone application was performed in May and June 1984” (Lusardi and Erickson, 1985, p. 318). These authors also conclude that “one year after the limestone application, the water quality in the seeps reflected no substantial inhibition or neutralization. Improvements in water quality noted in late 1984 have not persisted.” pH shows marked improvement (less acidic water) from June 30, 1984 onwards. However, by April 5, 1986 the pH has returned to pre-treatment levels; these changes are in accord with the conclusions given above. Nevertheless, discharge also shows a change and fluctuates over a much larger range after the treatment date. It is doubtful whether this can be attributed to the treatment.

The time series plot for acidity (Figure 5.7b) fluctuates above the mean up to the 50th observation and then becomes much less variable until just beyond the 70th observation. There is a large spike of increased acidity at 75 and then acidity declines back to the mean value from the 90th observation onwards.

In the case of total iron, the first 19 observations vary closely around the mean of the entire series; then, from observation 20 to 45, total iron shows much larger fluctuations, way above the mean. From the 45th to 55th observation, the variations in concentration are suppressed and from 55th observation onwards, the variability increases but remains around the mean value. Sulfate varies roughly in parallel with acidity and no special effect can be attributed to treatment.

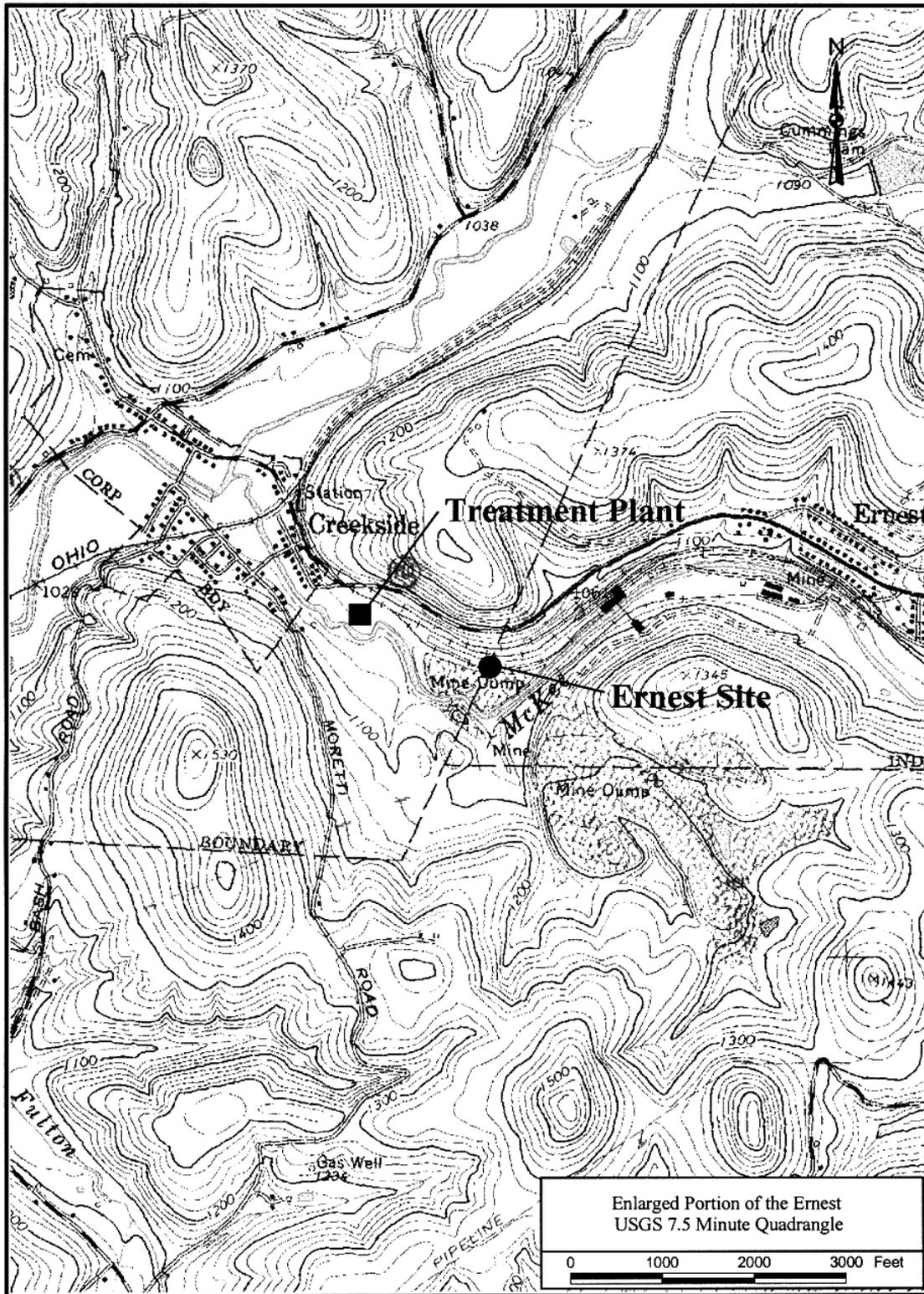
Chapter 6: Analysis of Data from Ernest Refuse Pile Site, Indiana County, PA

The Ernest mine site is located in the Crooked Creek watershed in Indiana County, PA near the town of Ernest (see Figure 6.0). The U.S. Army Corps of Engineers (USACE) completed construction of Crooked Creek dam in 1940 and has managed the lake since then for flood control and recreational purposes. The Commonwealth of Pennsylvania constructed and operated Crooked Creek State Park at the lake prior to 1981 when the USACE acquired the facility. Some portions of the Crooked Creek watershed were impacted by acid mine drainage from extensive bituminous coal mining, particularly the McKee Run tributary, from the town of Ernest downstream to the town of Creekside at the confluence with the main stem of Crooked Creek. The Ernest mine complex, including a large underground mine and associated coal refuse pile, was operated from the early 1900's to 1965 when the mine was abandoned.

An acid mine drainage treatment plant was constructed by the Pennsylvania Department of Environmental Protection and operated from June 1978 until May 1980 when problems with iron sludge recycling operations led to the closure of the plant. The water quality samples and flow measurements from the Ernest refuse pile discharge that are discussed in this chapter were collected between March 1981 and December 1985 as part of studies to evaluate water quality and aquatic biology in the Crooked Creek watershed following closure of the treatment plant. The raw data are listed in Appendix D. There are 198 observations ($N = 198$), consisting of values for 10 parameters: 1) Days (developed from the date that the sample was taken); 2) pH; 3) Flow; 4) Acidity; 5) Acid load; 6) Total Iron (Fe); 7) Total Iron load; 8) Ferrous Iron (FFe); 9) Sulfate (SO_4); 10) Sulfate load.

There is a rather large time gap (four months) between the first three observations and the remainder of the samples that were collected at approximately weekly intervals. There were also at least 15 samples without pH and/or ferrous iron data. After these samples were omitted and other adjustments were made (see Figure 3.1), a revised data set of 174 observations was compiled and used for most of the statistical analyses presented in this chapter. Time gaps in the data should be considered in examining the time series analyses, because elements of the time series analysis assume that there are equal intervals between observations.

Figure 6.0: Map of Ernest Mine Site



Univariate Analysis

Summary statistics for the adjusted data (N = 174) are presented in Table 6.1.

Table 6.1: Summary Statistics of Data (N=174)

	N	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Days	174	985.6	1027.0	995.3	457.2	34.7
pH	174	2.5061	2.5000	2.5018	0.1524	0.0116
Flow	174	127.2	51.0	85.9	337.0	25.5
Acidity	174	3621	3539	3585	1357	103
Acid Load	174	3367	1843	3031	3639	276
Total iron	174	527.2	515.5	520.5	210.0	15.9
Iron Load	174	626.6	275.0	563.1	722.3	54.8
Ferrous Iron	174	364.8	360.5	351.5	251.9	19.1
SO ₄	174	3887.4	3804.0	3915.5	1105.2	83.8
SO ₄ Load	174	3837	2108	3431	4198	318

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Days	0.0	1735.0	703.0	1343.5	46.4
pH	2.1	3.1	2.4	2.6	6.1
Flow	2.0	3188.0	8.0	163.2	265.0
Acidity	778	16401	3016	4301	37.5
Acid Load	111	17663	412	5641	108
Total iron	20.0	1929.0	395.0	653.0	39.8
Iron Load	10.0	2758.0	50.5	1147.7	115
Ferrous Iron	8.0	1760.0	161.5	512.0	69.1
SO ₄	142.0	6115.0	3155.0	4759.5	28.4
SO ₄ Load	117	17746	513	6394	109

The coefficient of variation (CV%) remains within fairly reasonable limits for pH, acidity, and iron. However, variability in ferrous iron (69%) is large. Sulfate is in reasonable control (CV = 28%). Flow, acid load, iron load, and sulfate load show very large variability (all greater than CV = 100%) which suggests that the large variability of the load-type variables is largely due to the high degree of variability shown by flow. These parameters require log transformation to control this variability. The frequency distribution of pH is symmetrical (Figure 6.1a) while flow is skewed, although the major part of the skewness arises from two extremely high values (Rows 142-3 in Appendix Table D, flow = 3003.0 gpm and 3188.0 gpm respectively). All other values of this parameter range from less than 10 to hundreds. Similarly, acidity has an extremely high value (Appendix D Table, Row 143 = 16,401 mg/L); acid load (Figure 6.1b) is skewed.

Total iron and total iron load follow the same pattern. Ferrous iron has one exceptional value. Sulfate (Figure 6.1f) is negatively skewed, whereas sulfate load is positively skewed. This behavior is an indication of the effect that flow can have on a parameter.

Table 6.2: Summary Statistics of Data (N=174)

	N	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Days	174	985.6	1027.0	995.3	457.2	34.7
pH	174	2.5061	2.5000	2.5018	0.1524	0.0116
Log Flow	174	1.6062	1.7076	1.6081	0.6970	0.0528
Log Acidity	174	3.5349	3.5489	3.5440	0.1466	0.0111
Log Acid Load	174	3.1854	3.2654	3.1930	0.6138	0.0465
Log Total Iron	174	2.6836	2.7122	2.6997	0.2066	0.0157
Log Iron Load	174	2.3564	2.4393	2.3703	0.7244	0.0549
Log Ferrous Iron	174	2.3989	2.5569	2.4442	0.4696	0.0356
Log SO ₄	174	3.5646	3.5802	3.5815	0.1748	0.0133
Log SO ₄ Load	174	3.2403	3.3240	3.2480	0.6143	0.0466

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Days	0.0	1735.0	703.0	1343.5	46.4
pH	2.1000	3.1000	2.4000	2.6000	6.1
Log Flow	0.3010	3.5035	0.9031	2.2127	43.4
Log Acidity	2.8910	4.2149	3.4795	3.6336	4.1
Log Acid Load	2.0453	4.2471	2.6149	3.7514	19.3
Log Total Iron	1.3010	3.2853	2.5966	2.8149	7.7
Log Iron Load	1.0000	3.4406	1.7032	3.0598	30.7
Log Ferrous Iron	0.9031	3.2455	2.2082	2.7093	19.6
Log SO ₄	2.1523	3.7864	3.4990	3.6776	4.9
Log SO ₄ Load	2.0682	4.2491	2.7098	3.8058	18.9

Summary statistics for log (base 10) transformed data are listed in Table 6.2 (N = 174). The variables are now either well-behaved ($CV \leq 20\%$) or are not too extreme ($CV \leq 50\%$). Load variables show the largest CV%. This is most likely largely due to flow variability.

Histograms of the log transformed data are displayed in Figures 6.1c, 6.1e, and 6.1g. By plotting the histograms of the original data alongside that of the transformed data, the effect of the transformation is clear. Because pH is already expressed in logarithms, no transformation was applied. In all other parameters, log transformation expanded low magnitude values and reduced asymmetry (for acid load in Figures 6.1b and 6.1c), sometimes perhaps, too much (Figures 6.1d

and 6.1e, iron and log iron respectively). Similarly, because the histogram of sulfate is negatively skewed, log transformation accentuated the negative skewness (Figures 6.1f and 6.1g) making log transformation unnecessary. All load variables are strongly positively skewed when untransformed and the log transformation helps to improve their symmetry.

Figure 6.1a: Histogram of pH, (N = 174)

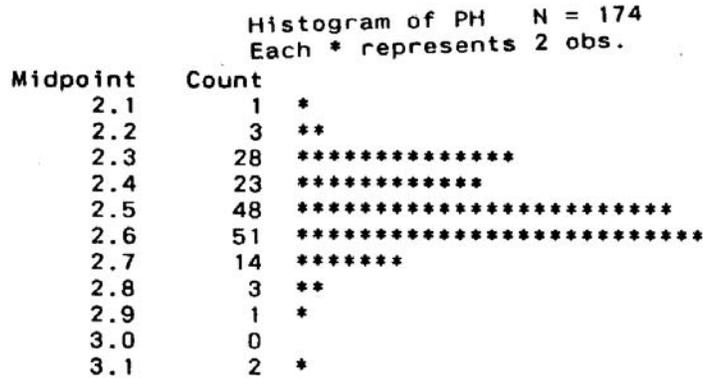


Figure 6.1b: Histogram of Acid Load, (N = 174)

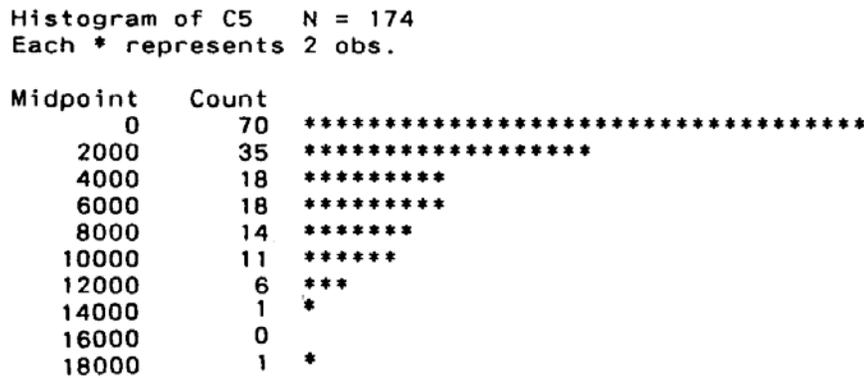


Figure 6.1c: Histogram of Log Acid Load (N=174)

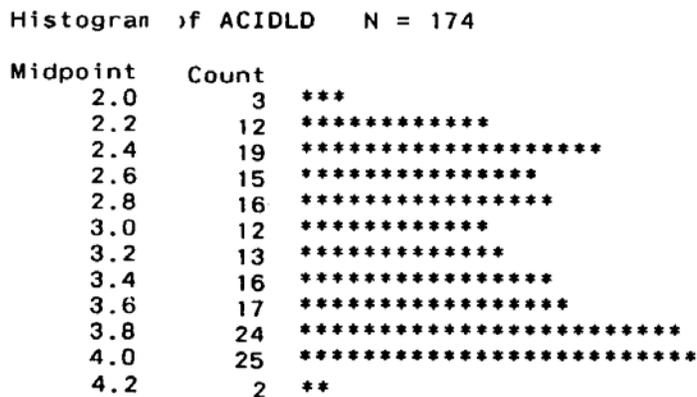


Figure 6.1d: Histogram of Total Iron (N=174)

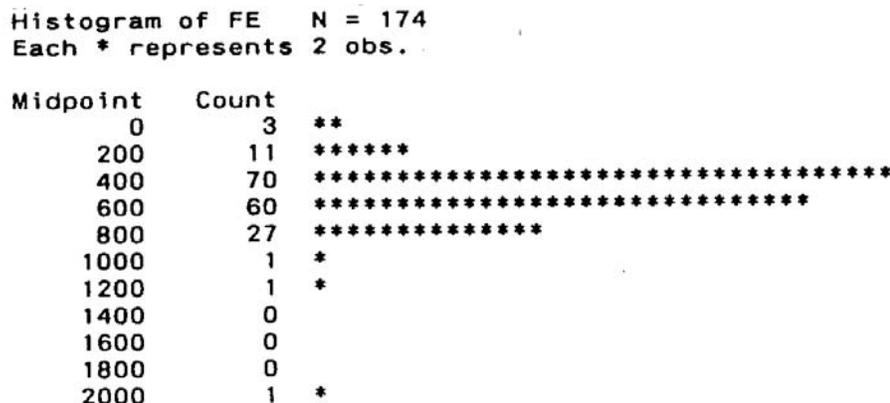


Figure 6.1e: Histogram of Log Total Iron (N=174)

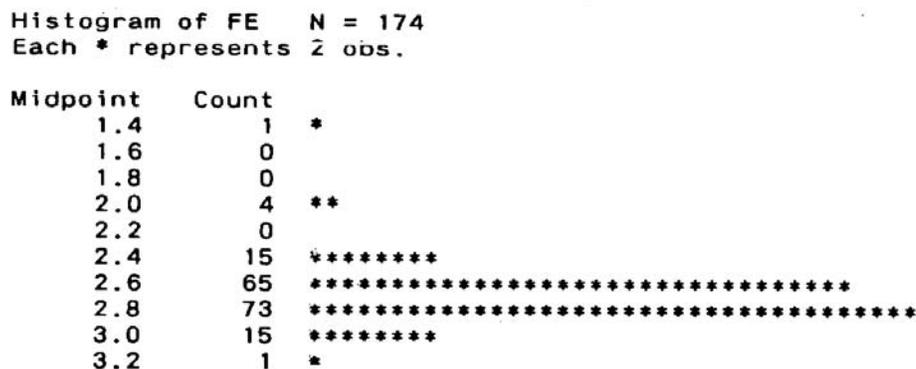


Figure 6.1f: Histogram of SO₄ (N=174)

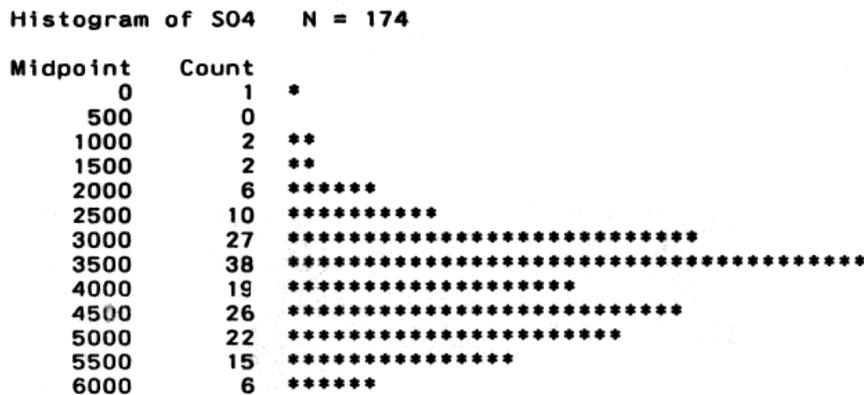
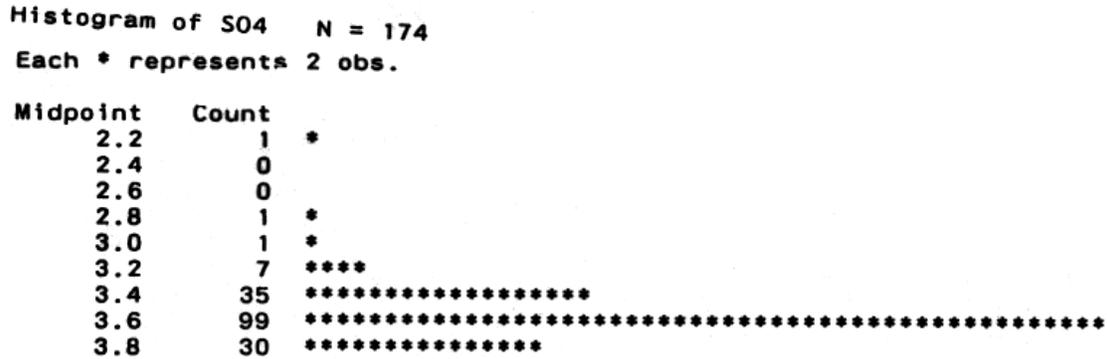


Figure 6.1g: Histogram of Log SO₄ (N=174)



Bivariate Analysis

The bivariate statistical analysis of the Ernest data includes bivariate plots (routinely used in regression and correlation analyses), the use of a correlation matrix to compare and evaluate correlation coefficients, and the use of cross correlation functions to determine if lags in the data for certain parameters tend to obscure correlations that may be present. The correlation matrix is an element of some multivariate statistical analyses, such as principal components analysis and factor analysis (in the r mode). The cross-correlation function is an element of time series analysis because it computes and graphs correlations between two time series. Both of these statistical tools are included in this discussion of bivariate analysis because they are useful in examining the relationship between pairs of variables.

The correlation coefficients for all pairs of variables are shown in Table 6.3. The correlation coefficient (r) at the five percent probability level is given above the table and all correlation coefficients larger than this number are significantly different from zero. For example, only iron vs. pH (r = 0.124) is not significantly different from zero. Similarly, ferrous iron vs. acidity (r = 0.045) and sulfate vs. ferrous iron (r = 0.083) are also not significantly different from zero. All other coefficients reflect a real association (statistically significant), however, in many cases, the degree of association (r² x 100%) is small. For example, the correlation of acidity and pH (r = -0.365) indicates an inverse linear association between the two variables as would be expected, but the degree of association is small (r² = 13%).

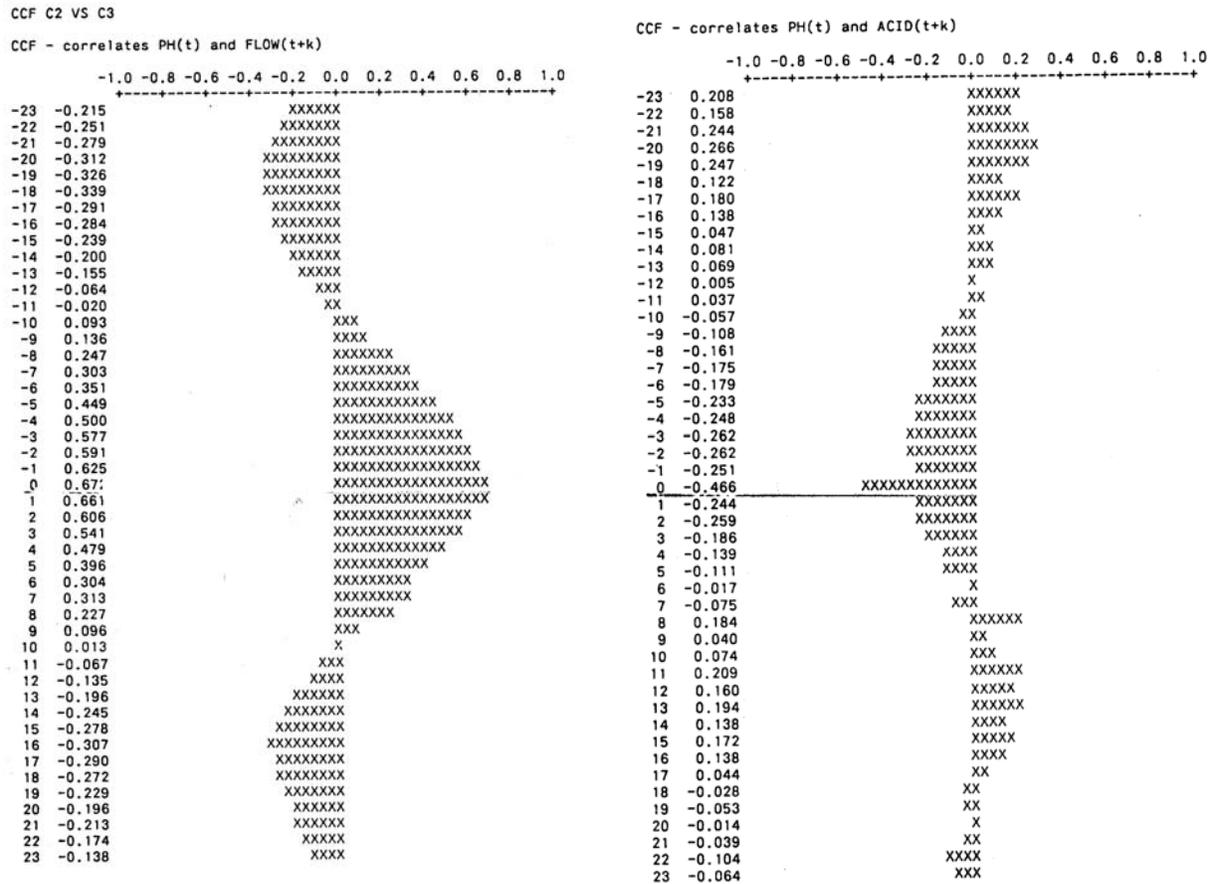
Table 6.3: Correlation Coefficients for 9 Parameters (N=174, $r_{0.05} = 0.159$)

	pH	Flow	Acid	Acid Load	Total Iron	Iron Load	Ferrous Iron	SO ₄
Flow	0.191							
Acidity	-0.365	0.308						
Acid Load	0.483	0.206	-0.224					
Total Iron	0.124	0.337	0.526	0.263				
Iron Load	0.498	0.229	-0.262	0.913	0.375			
Ferrous iron	0.248	-0.020	0.045	0.337	0.480	0.388		
SO ₄	-0.547	-0.184	0.600	-0.307	0.174	-0.339	0.083	
SO ₄ Load	0.472	0.438	-0.030	0.906	0.386	0.890	0.285	-0.293

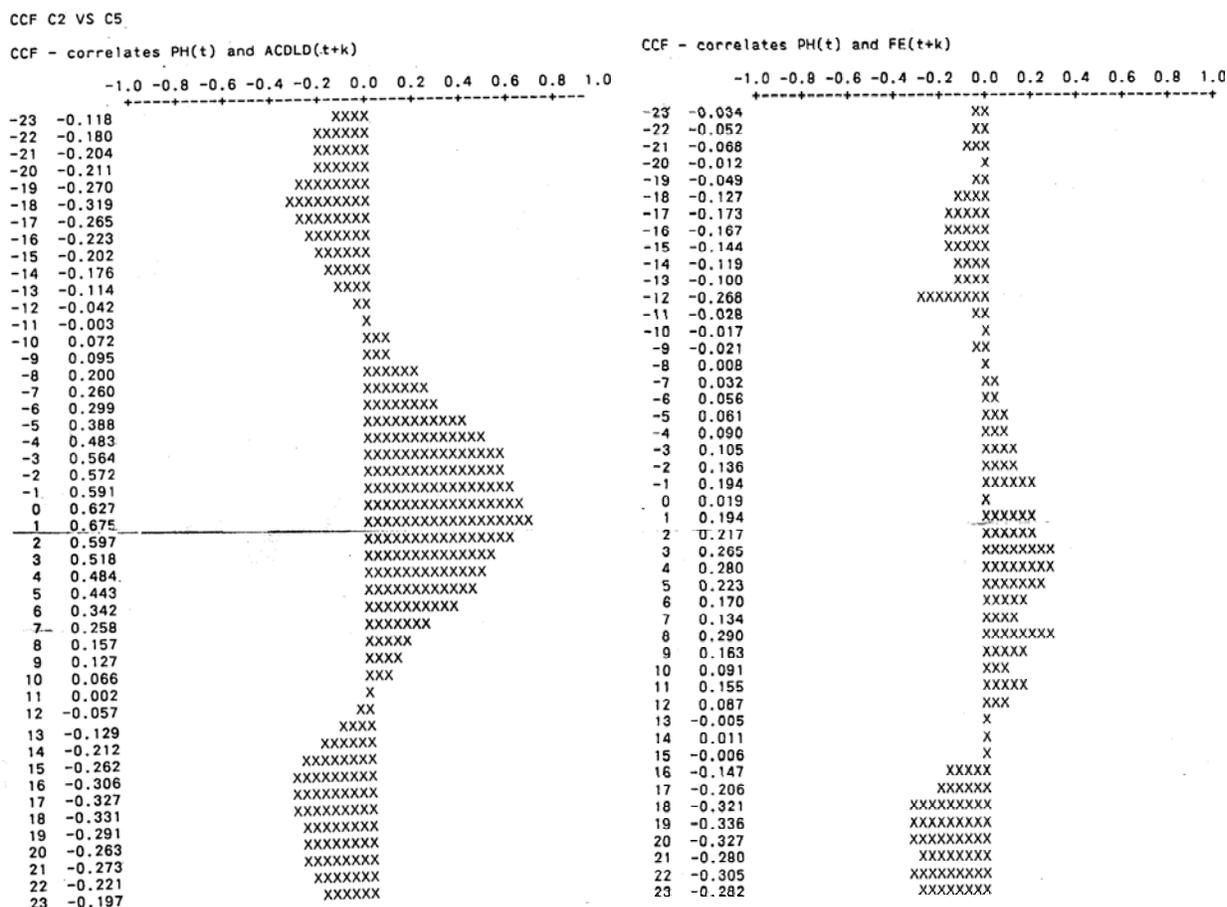
There are three large correlation coefficients between acid load vs. iron load, acid load vs. sulfate load, and iron load vs. sulfate load. These correlation coefficients are all around $r = 0.9$ (i.e., about 80 percent in common), probably because of the domination of flow in the measurement of load variables. Whereas, the individual concentration variables acidity vs. iron ($r = 0.526$), acidity vs. sulfate ($r = 0.6$), and iron vs. sulfate ($r = 0.174$) show much lower association (the largest r^2 is 36 %). In addition, any load variable vs. concentration of the same variable shows no appreciable relationship. Thus, the relatively high correlation coefficients due to the inclusion of flow in all load variables is an artifact from the calculation for load (concentration x 0.01212 x flow).

When one examines the cross-correlation functions (Figures 6.2a to 6.2d), it can be seen that the largest correlation occurs at lag zero in Figure 6.2a (pH vs. log flow) and at lag one in Figure 6.2c (pH vs. log acid load) and that the correlations are of the same order of magnitude. Because pH vs. log acidity (Figure 6.2b) yields the strongest $r = -0.466$ at lag zero, which is much weaker than the value yielded by pH vs. acid load (Figure 6.2c), it is suspected that the effect of flow on load is responsible for the higher correlation. The highest correlation in Figure 6.2d (pH vs. log iron) occurs at lag 19 ($r = -0.336$), but values of $r > 0.25$ occur haphazardly at many lags and any association is likely to be very weak.

Figures 6.2a and 6.2b: Cross Correlation Functions of pH vs. Log Flow, and pH vs. Log Acid (respectively)



Figures 6.2c and 6.2d: Cross Correlation Functions of pH vs. Log Acid Load, and pH vs. Log Iron (respectively)



When either pH (which is a logarithmic measure) or logarithms of the other parameters are plotted against days, they appear to show periodic variation with a very large degree of scatter (see for example, pH vs. days (Figure 6.3a) and log flow vs. days (Figure 6.3b)). Log acidity vs. days was not as evident, but log acid load vs. days (Figure 6.3c) is clearly periodic. Here again, the effect of flow on load is likely to be responsible for the cyclical appearance.

Figure 6.3a: Plot of pH vs. Time (days)

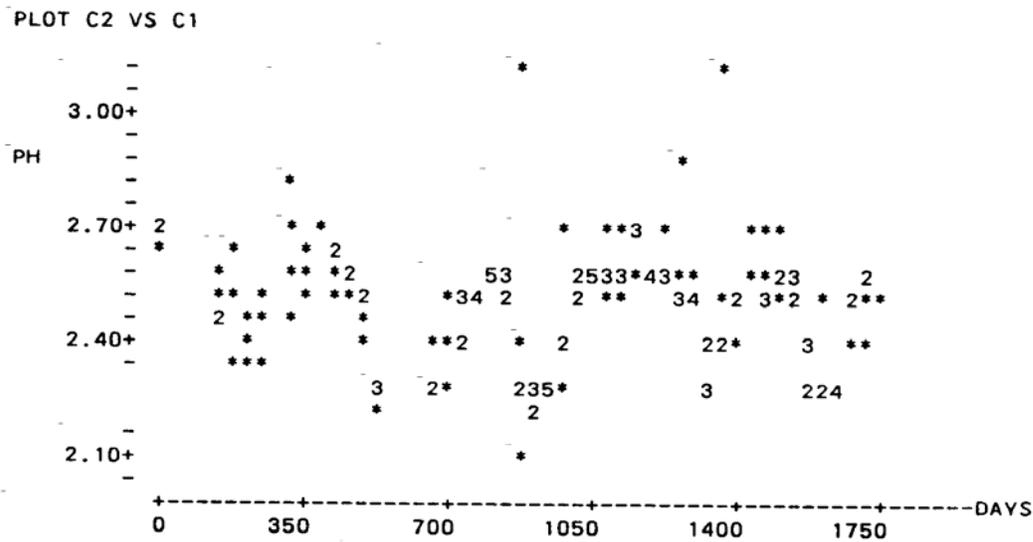


Figure 6.3b: Plot of Log Flow vs. Time (days)

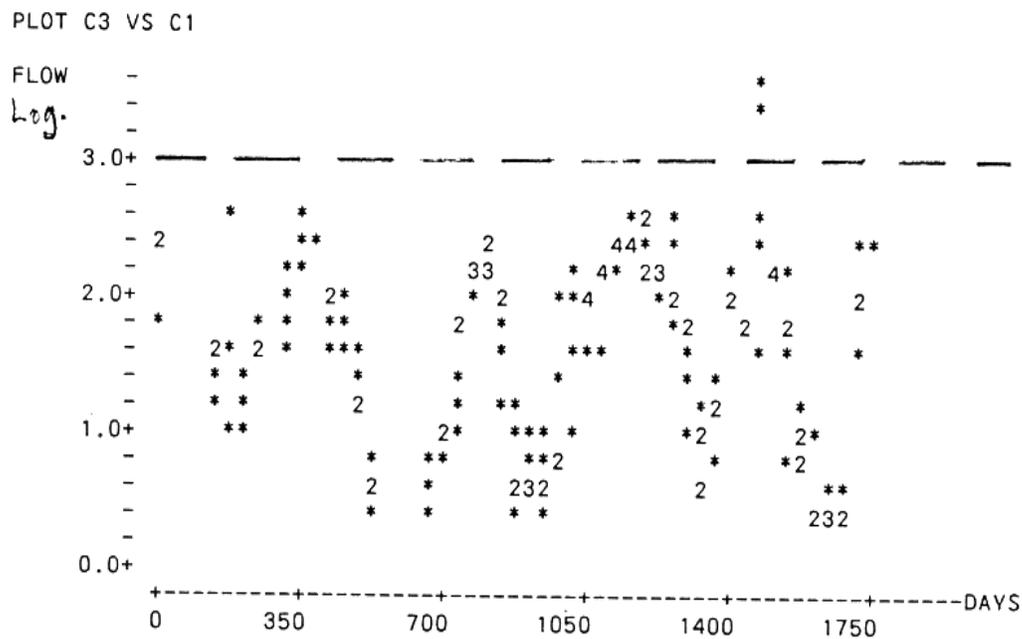
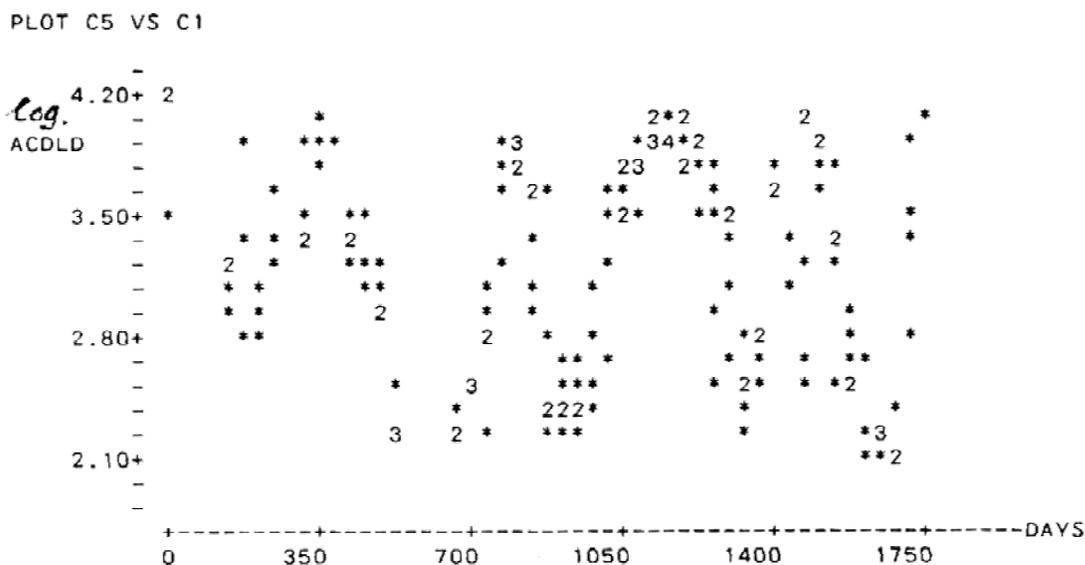


Figure 6.3c: Plot of Log Acid Load vs. Time (days)



Bivariate plots of untransformed data were made and it was found that in most cases, there was little relationship between concentration and load (e.g., Figure 6.4, acidity vs. acid load). The only discrepancies are extreme values which occur as outliers (e.g., observation 158).

Figure 6.4: Plot of Acid vs. Acid Load

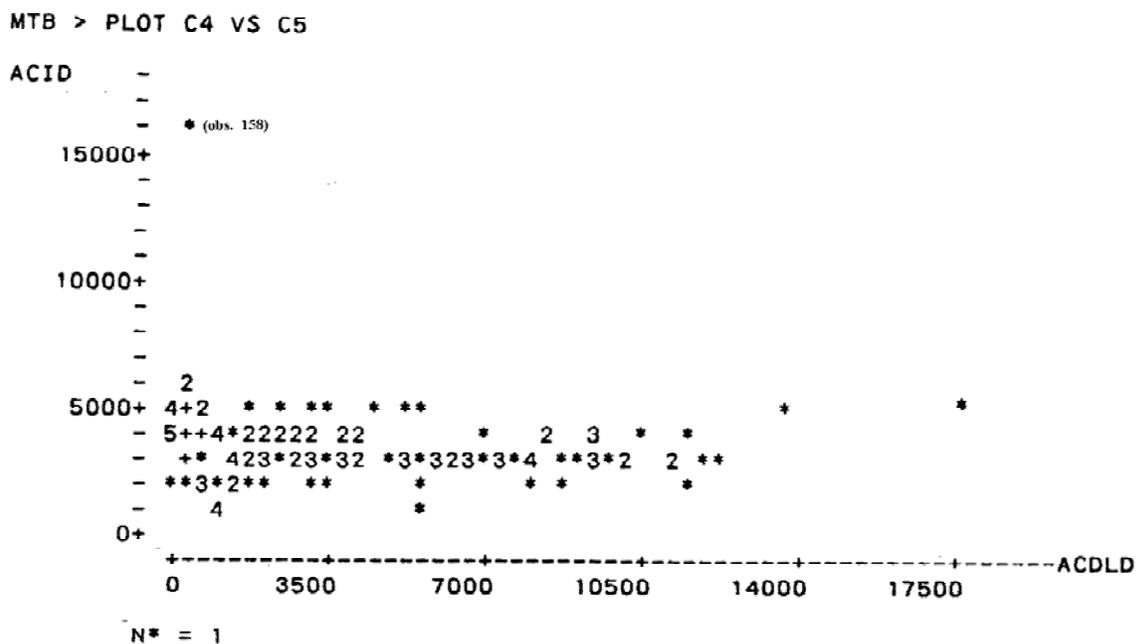


Figure 6.6b: Bivariate Plot of Log Sulfate vs. Log Flow

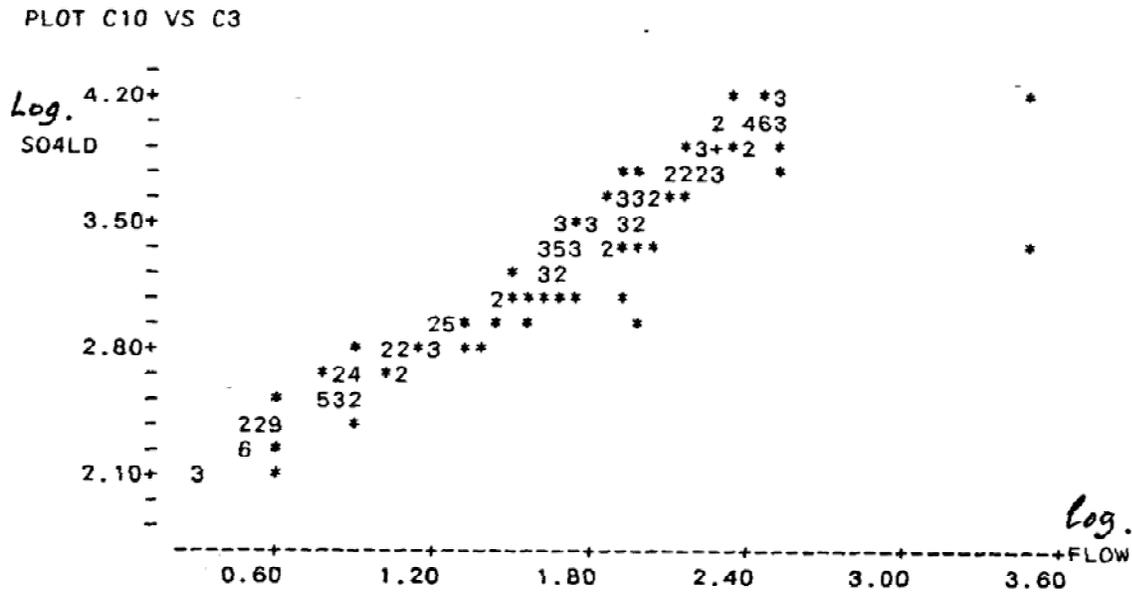


Figure 6.6c: Bivariate Plot of Log Acidity vs. Log Acid Load

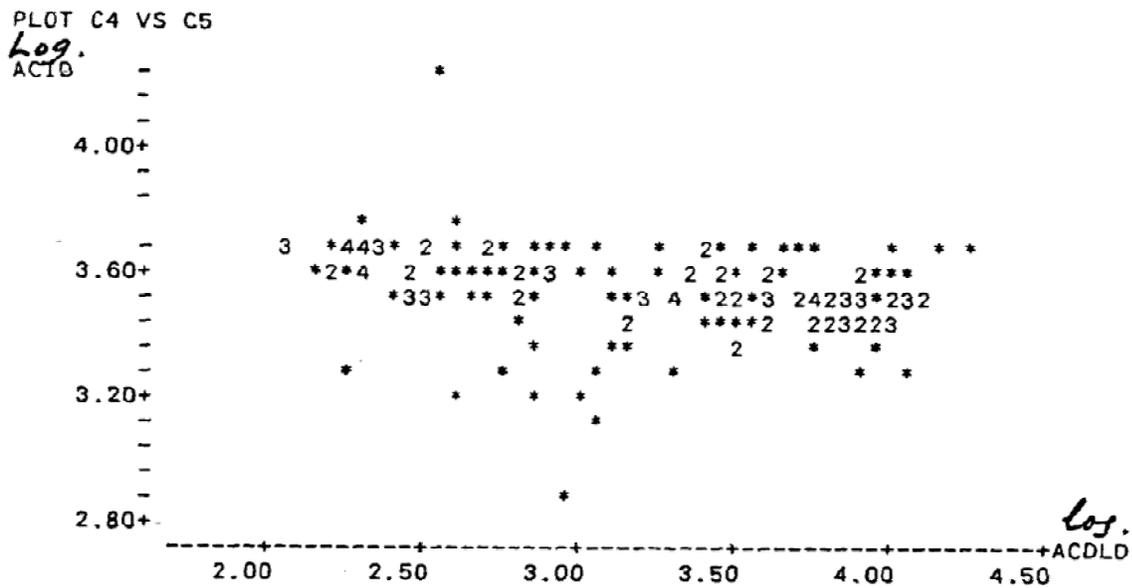


Figure 6.7a: Time Series Plot of pH

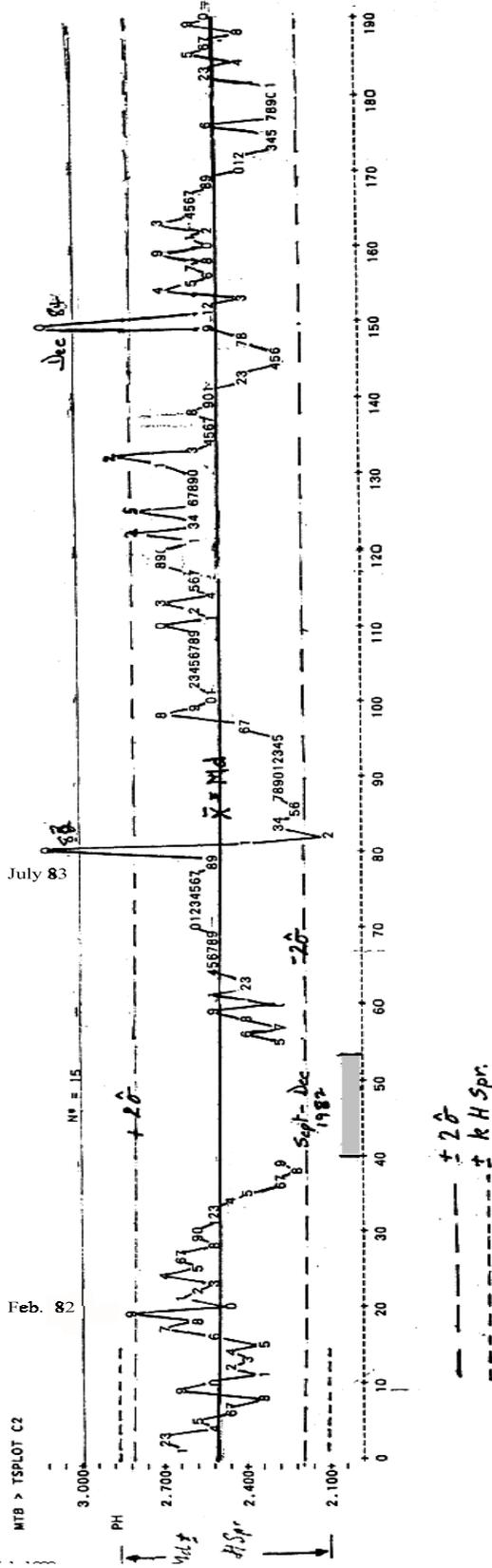


Figure 6.7b: Time Series Plot of Flow

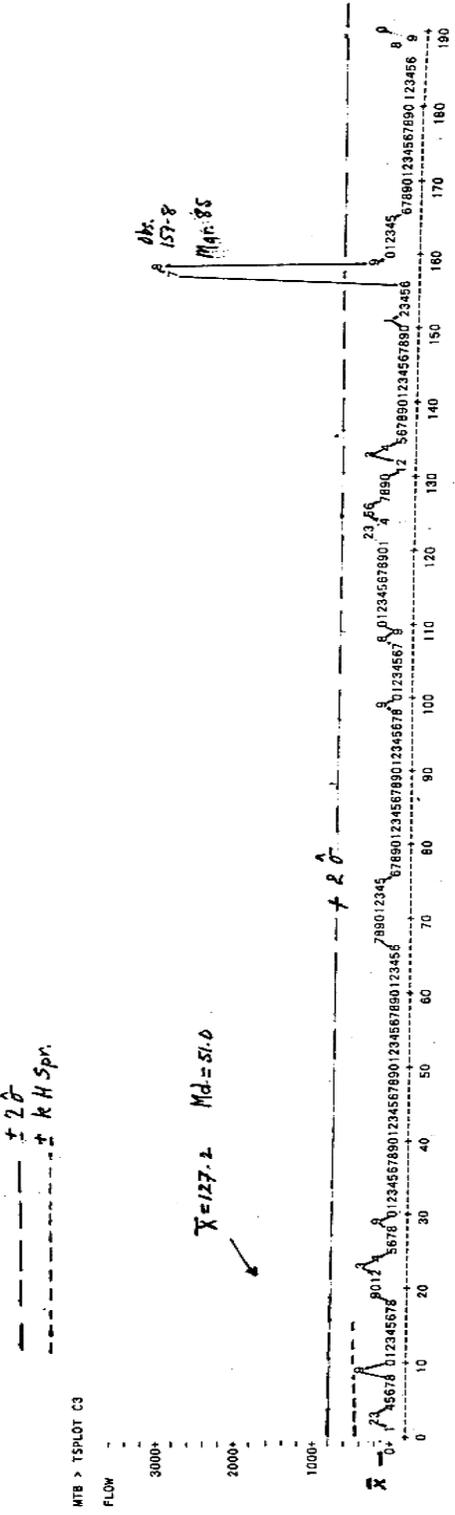


Figure 6.7e: Time Series Plot of Acid Load

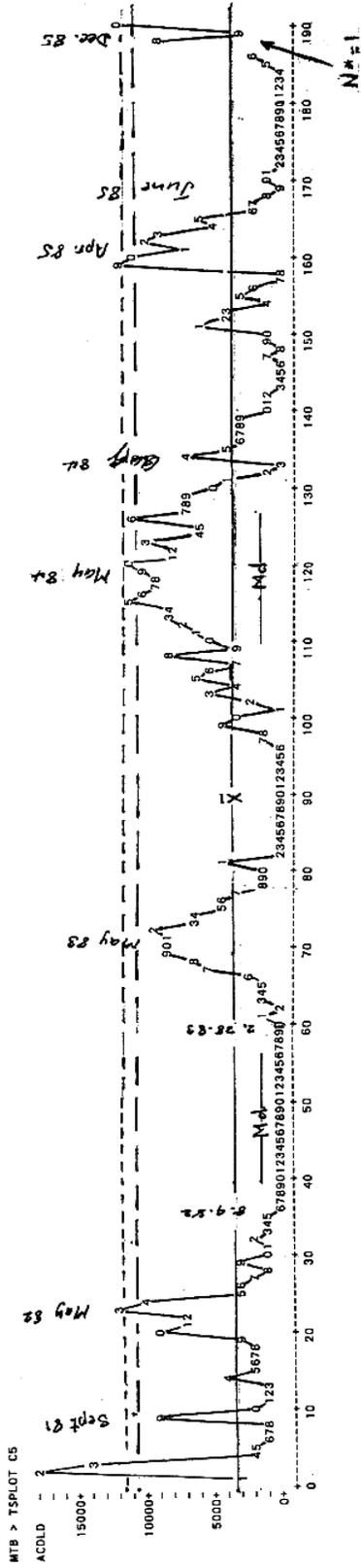
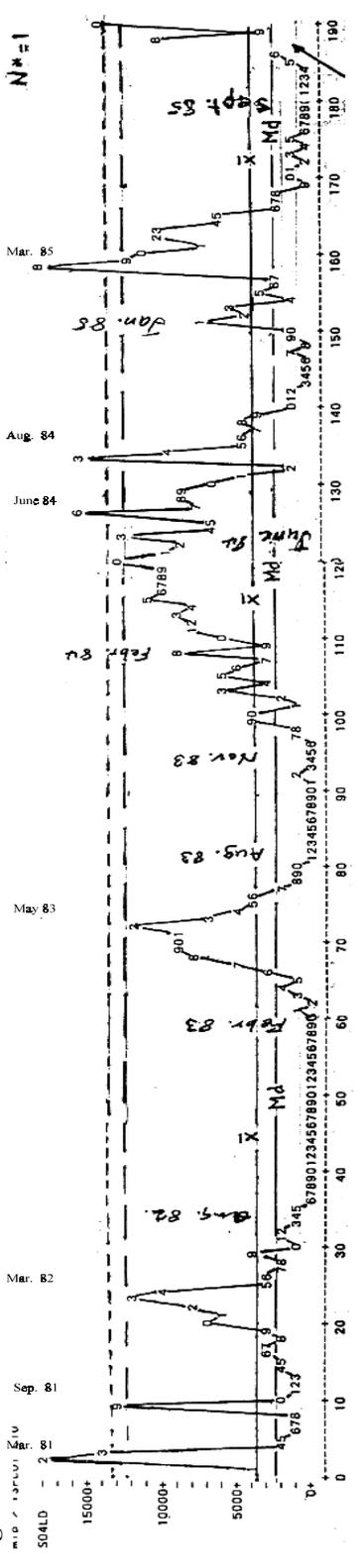


Figure 6.7f: Time Series Plot of Sulfate Load



Quality Control Limits for the Variables

Two measures of quality control were used to illustrate this aspect of the analysis. The first is conventional (mean $\pm 2\sigma$ the standard deviation). The second is non-parametric (median ± 1.96 x a function of the H-spread). Since sample size, $N' = 1$, the function is: $(1.25 * \text{H-Spread} / 1.35)$. Both measures are based on analysis of the Clarion data (“Quality Control Limits,” Chapter 5). Summary statistics for these measures are listed in Tables 6.4 and 6.5. At the base of each table are statistics for the three load variables expressed in logarithms.

Table 6.4: Base Data for Calculation of Quality Control Limits of Ernest Data

No.	Variable	Mean \bar{X}	Median	R = H-spread	C-spread	$\hat{\sigma}$	H-spread/1.345
2.	pH	2.506	2.50	0.2	0.530	0.1524	0.148
3.	Flow	127.2	51.0	153.0	342.0	337.0	113.4
4.	Acid	3621.	3539.	1283.	3493.	1357.	951.1
5.	Acid Load	3367.	1843.	5210.	11307.	3639.	3862.1
6.	Total Iron	527.2	515.5	358.	647.	210.	265.4
7.	Iron Load	626.6	275.0	1096.	2193.	722.3	812.5
8.	Ferrous Iron	364.8	360.5	348.	807.	251.9	258.
9.	SO ₄	3887.4	3804.	1583.	3933.	1105.2	1173.5
10.	SO ₄ Load	3837.	2108.	5857.	13711.	4198.	4341.7
Log. Data							
5.	Log Acid Load	3.120	3.265	1.127	1.869	0.631	0.835
7.	Log Iron Load	2.277	2.439	1.352	2.168	0.747	1.002
10.	Log SO ₄ Load	3.175	3.324	1.089	1.917	0.632	0.807

Table 6.5: Two Measures of Quality Control (1) $\pm 2 \hat{\sigma}$

$$(2) 1.96 [(1.25 \text{ H-spread}) / 1.35 \sqrt{N'}]$$

No.	Variable	Mean (\bar{X})	$\bar{X} \pm 2 \hat{\sigma}$	Md $\pm 1.96(\dots)$	$1.96 [(1.25 \text{ H-spread}) / 1.35 \sqrt{N'}]$	Median	$2 \hat{\sigma}$
2.	pH	2.506	2.201 to 2.811	2.137 to 2.863	0.363	2.500	0.305
3.	Flow	127.2	-546.8 to 801.2	-226.7 to 328.7	277.7	51.0	674.0
4.	Acid	3621	907 to 6335	1211 to 5867	2328	3539	2714
5.	Acid Load	3367	-3911 to 10645	-7612 to 11298	9455	1843	7278
6.	Total Iron	527.2	107.2 to 947.2	-134.2 to 1165.2	649.7	515.5	420.0
7.	Iron Load	626.6	-818.0 to 2071.2	-1714.0 to 2264.0	1989.0	275.0	1444.6
8.	Ferrous Iron	365	-139 to 868.6	-271 to 992	632	361	504
9.	SO ₄	3887.4	1677.0 to 6097.8	931.1 to 6676.9	2872.9	3804.0	2210.4
10.	SO ₄ Load	3837	-4559.0 to 12233.0	-8521.4 to 12737.4	10629.4	2108.0	8396.0

No.	Variable	Mean (\bar{X})	$\bar{X} \pm 2 \hat{\sigma}$	Md \pm 1.96(..)	1.96 [(1.25 H- spread)/ 1.35 $\sqrt{N'}$]	Median	2 $\hat{\sigma}$
Log. Data							
5.	Log Acid	3.120	1.858 to 4.382	1.220 to 5.310	2.045	3.265	1.262
7.	Log Iron	2.277	0.783 to 3.771	-0.015 to 4.893	2.454	2.439	1.494
10.	Log SO ₄	3.175	1.911 to 4.439	1.348 to 5.300	1.976	3.324	1.264

These two quality control limits are inserted as dashed lines in Figures 6.7a through 6.7f. For pH (Figure 6.7a), similar limits resulted from both measures. The mean and median coincide (on the scale of the graph in Figure 6.7a), and frequency distribution of pH is essentially symmetrical.

For flow and acidity (Figures 6.7b and 6.7c respectively), the standard deviations are inflated by rare extreme values. Thus, the quality control limits for both measures are essentially insensitive except to the extremes. It should be noted that the range is small.

The quality control limits for the load variables are wide, with the lower limits falling below zero. The lower limits are, therefore, omitted from the graphs (Figures 6.7d through 6.7f). The respective means and medians are not very different in magnitude and neither are the positive control limits. The use of either quality control limit would have little effect in identifying exceedences of baseline pollution load. It appears from these graphs that either measure would suffice. Sensitivity to departures from set limits could be increased by dividing by the square root of N' , or by increasing sample size (e.g., from 1 to 4). This would reduce the range to half its original value. On the other hand, use of the root N' factor with $N' > 1$, could increase the sensitivity too much and many values of these widely fluctuating parameters would fall outside the limits thereby calling for action. If fluctuations arise from “natural causes” and not from mining activity, this would be undesirable. Obviously, the entire range of pH, for example, is small (2.1 – 3.1) and the discharge is consistently acidic.

Model Identification

Autocorrelation functions form the basis for model identification in applying full-scale Box-Jenkins time series analysis. Hence, the autocorrelation and partial autocorrelation functions were run on the data for each variable. The graphs are presented in Figures 6.8a, 6.8b, 6.8c, 6.8e, and 6.8g, for the autocorrelation functions (Acf) and Figures 6.8d, 6.8f, and 6.8h for the partial autocorrelation functions (Pacf).

Figure 6.8a: Autocorrelation Function of pH

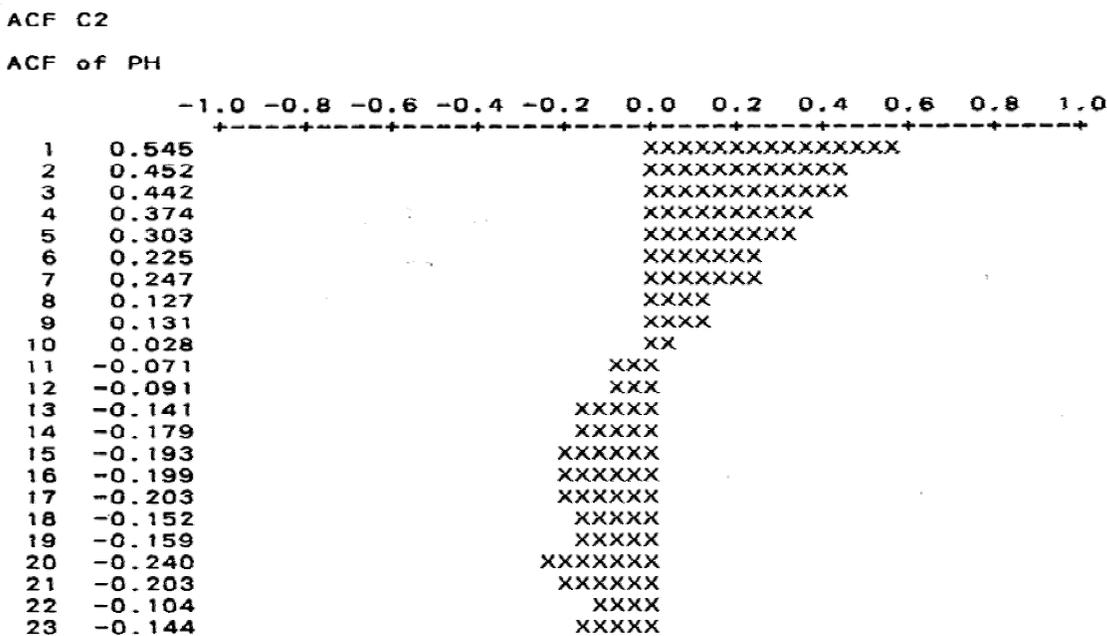


Figure 6.8b: Autocorrelation Function of Iron

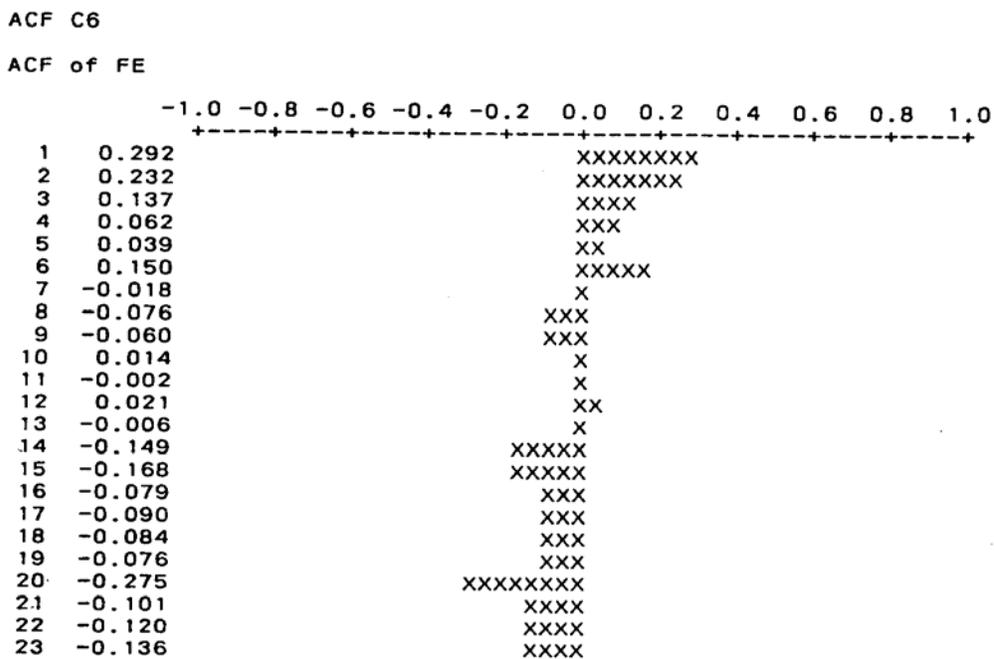


Figure 6.8c: Autocorrelation Function of Flow

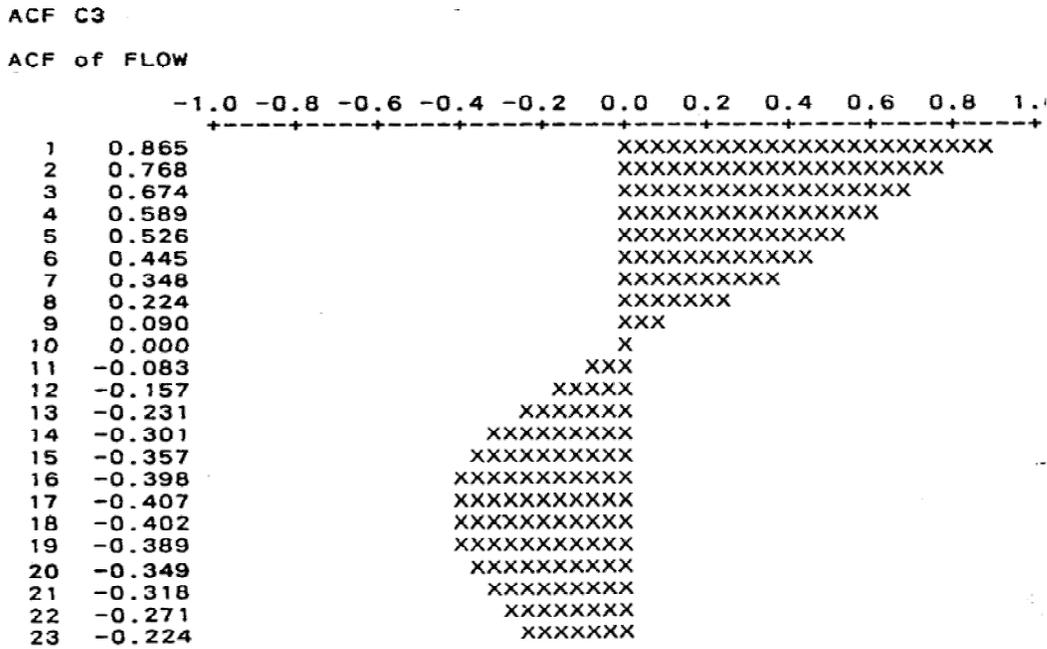


Figure 6.8d: Partial Autocorrelation Function of Flow

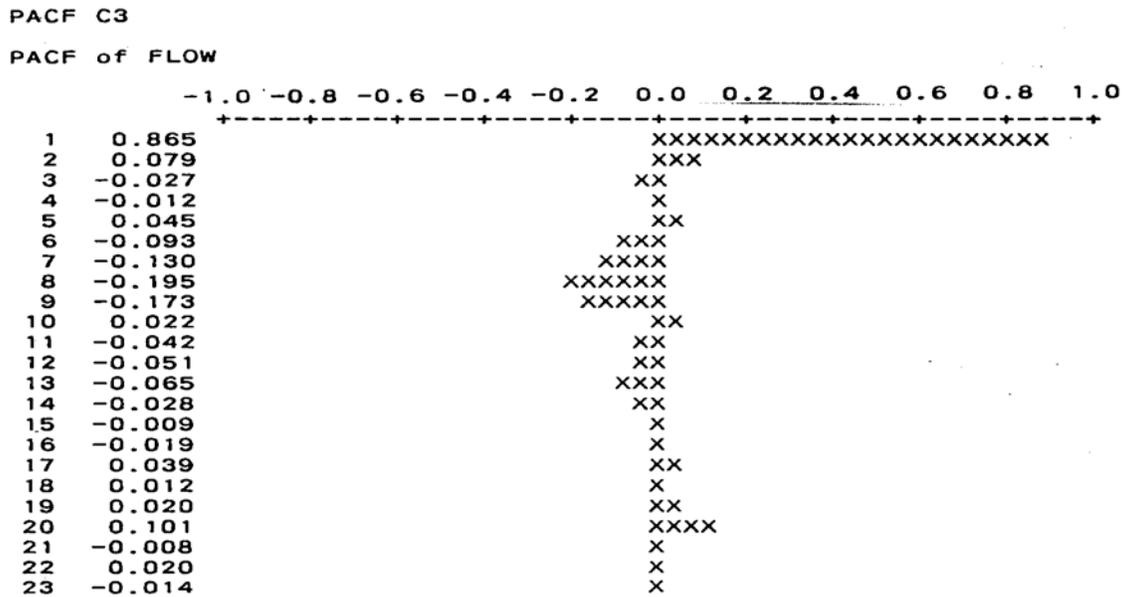


Figure 6.8e: Autocorrelation Function of Acidity

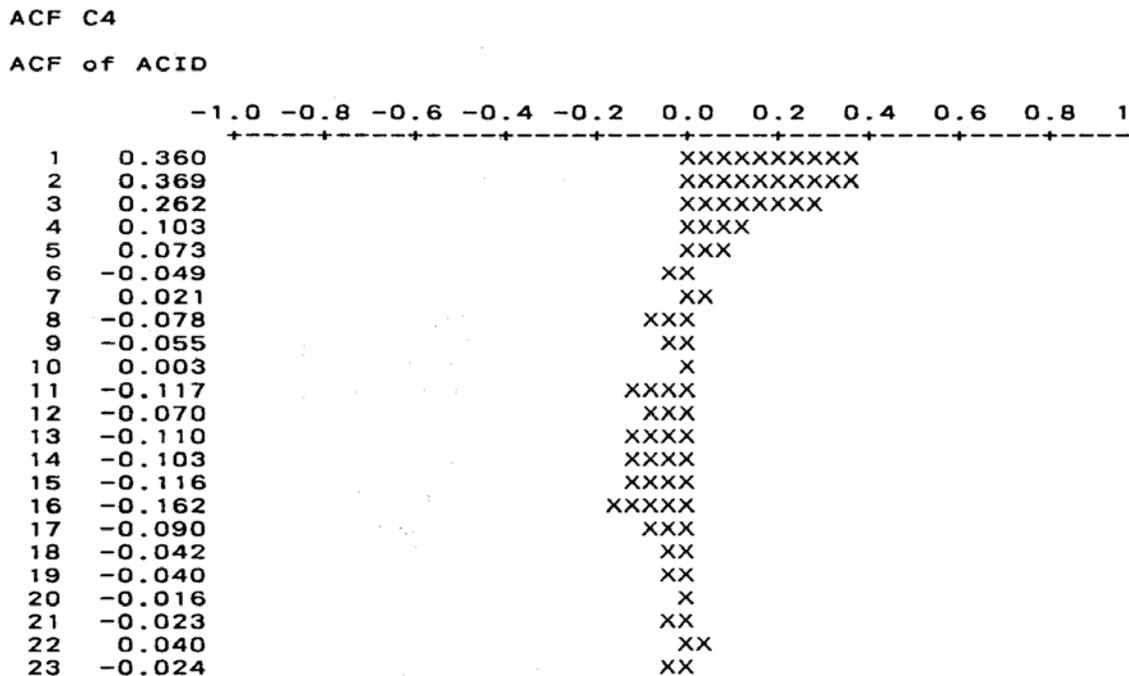


Figure 6.8f: Partial Autocorrelation Function of Acidity

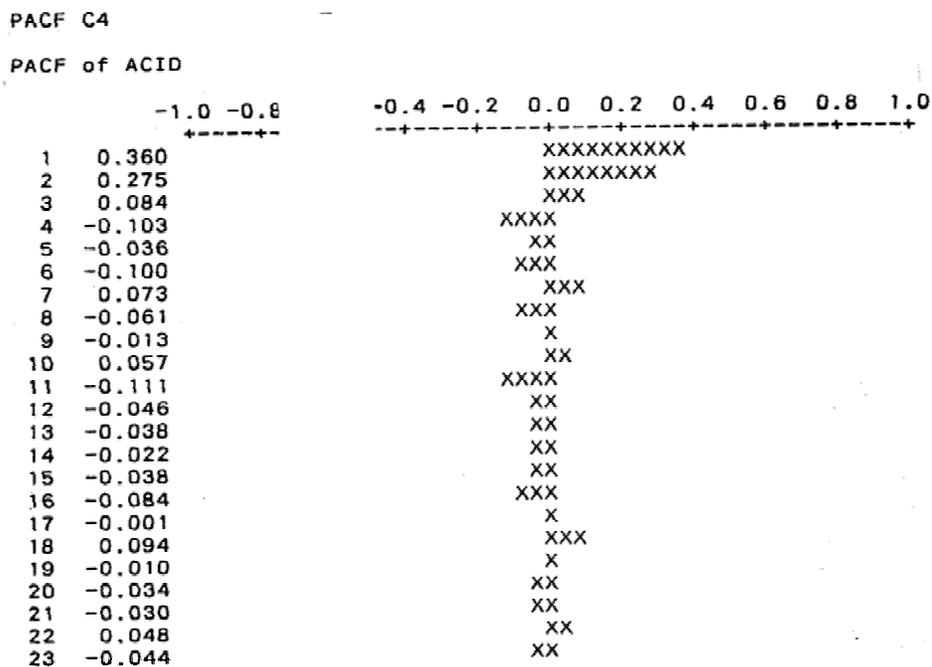


Figure 6.8g: Autocorrelation Function of Acid Load

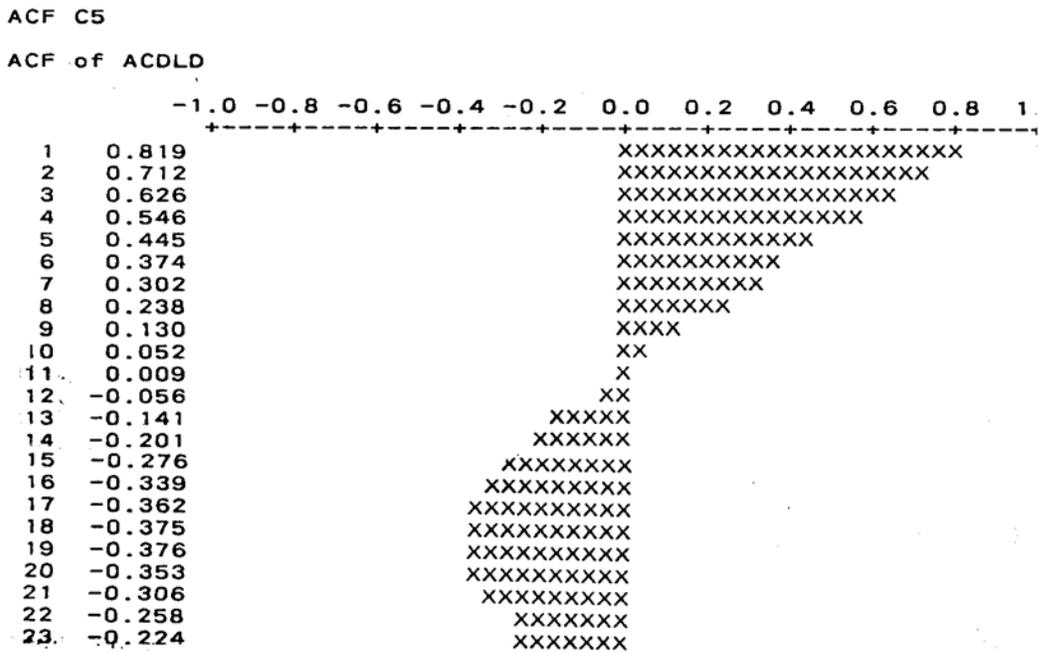
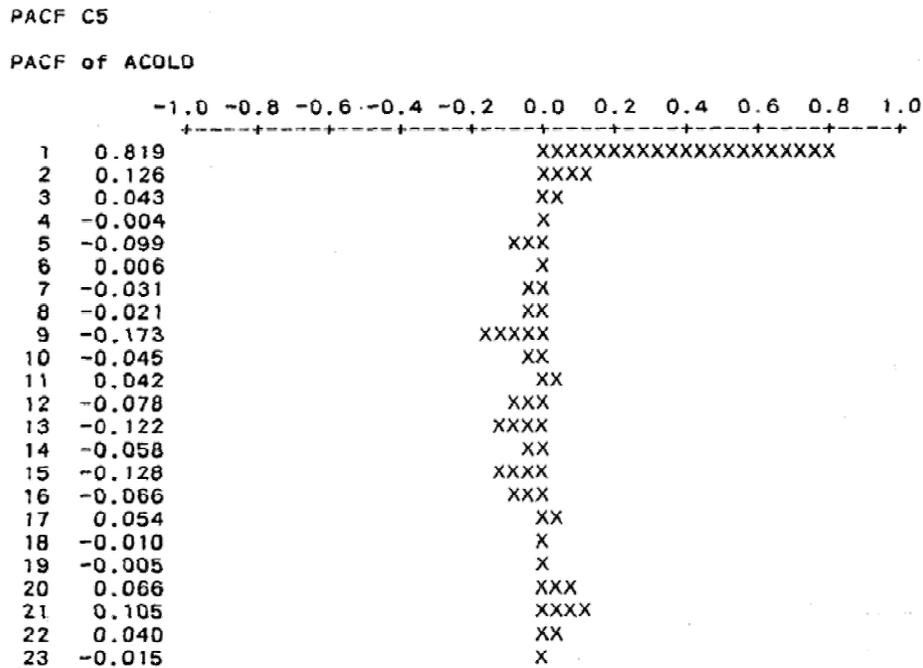


Figure 6.8h: Partial Autocorrelation Function of Acid Load



pH (Figure 6.8a), flow (Figure 6.8c), and three load parameters (e.g., see Figure 6.8g for acid load) yield similar Autocorrelation functions (Acf's). The concentration variables acidity (Figure 6.8e), iron (Figure 6.8b), and sulfate (Figure not available) also show similar Acf's, but the former set (which includes load) differs from the latter. The former set shows a strong decline throughout the function. This decline is confirmed by the single large spike at lag 1 in the corresponding partial autocorrelation factors (Pacf's, Figures 6.8d and 6.8h). This behavior implies that all these variables require a first difference to remove the trend. The Acf and Pacf for each of the concentration variables (e.g., Figures 6.8e and 6.8f) suggest moving average (MA) models with at most two terms (or one term and a first difference). It is perhaps advisable to try an auto-regressive moving average (ARMA) model in which the AR term could proxy for the first difference and the MA term would take care of the remainder.

Model Fitting: pH

It was decided to attempt to fit an auto-regressive integrated moving average (ARIMA) model (1,1,1) to variation in pH. The correlation coefficient between the AR and MA coefficients was $r = 0.81$, which implies that they are closely associated (i.e., both are unlikely to be necessary). Testing the Acf of the residuals yielded a chi-square = 27.16 with 28 degrees of freedom (i.e., the Acf is not significantly different from that of white noise). There is only one significant spike at lag 20 in this Acf, thus, it is effectively clean. Any further differencing results in overdifferencing (i.e., chi-square of the Acf increases to significant again). The model has improved the variation (Pacf of the residuals has no significant spikes) but contains an unnecessary coefficient $\hat{\Phi}_1$. Clearly, the AR (1) is adequately taken care of by the first difference.

If we now fit a moving average model with a first difference (i.e., an MA (0,1,1) model), the Acf of the residuals yields a chi-square of 26.87 with 29 degrees of freedom (thus, not significantly different from an Acf of white noise). Any further differencing overcompensates. The only significant spike is at lag 20 as in the previous model. Because this is an isolated significant autocorrelation way out from zero lag, it is considered a random discrepancy. The Pacf of the residuals is also clean. The 95% confidence limits around the MA coefficient ($\hat{\theta}_1$) does not contain zero. Hence, the MA coefficient is significantly different from zero (real) and, incidentally, about the same size as in the ARIMA model ($\hat{\theta}_1 = 0.594$). The residual standard deviation is $\hat{\sigma}_e = 0.126$, a reduction in the pH of the original data from 0.152 to 0.126. The relationship may be expressed as:

$$z_t = z_{t-1} + a_t - 0.594a_{t-1}$$

Model Fitting: Flow (Log)

An AR (1,0,0) model was fitted to the variation in logarithms of the flow variable; it was considered that the AR(1) coefficient would “take care of” the first difference. Chi-square of the residual = 30.06 with 28 degrees of freedom ($0.50 > P > 0.30$; i.e., not significantly different from that expected from white noise). There are no significant spikes in the Acf or Pacf values.

This model yields the following equation with standard deviation of the residuals $\hat{\sigma}_e = 0.347$ (reduced from 0.697 for the original standard deviation of the logarithms of flow in Table 6.2):

$$z_t = 0.873 z_{t-1} + 1.636 + a_t$$

Model Fitting: Acidity (Log)

From the Acf, developed during the identification step of the Box-Jenkins series, it was decided to try an MA (0,1,2) model which would presumably clear out the large spikes at the first three lags in the Acf. Upon fitting, it turned out that the correlation coefficient between the two moving average coefficients ($\hat{\theta}_1$ and $\hat{\theta}_2$) was -0.612 (i.e., as one increased the other decreased). A chi-squared test of the residual Acf yielded 29.86 with 28 degrees of freedom ($0.50 > P > 0.30$). The Acf spike at lag 6 is significantly larger than its error.

Upon testing the coefficients of this model, the $\hat{\theta}_1 = 0.642$ and is real, but the second $\hat{\theta}_2 = -0.640$ and its confidence belt included zero. The standard deviation of the residuals is 0.139.

An MA (0,0,2) model showed no correlation among the two coefficients or between either coefficient and the mean. The residual chi-square = 32.77, with 27 degrees of freedom ($0.30 > P > 0.20$) is not significantly different from that expected from white noise (random error). The relevant equation is:

$$z_t = 3.536 + a_t + 0.205a_{t-1} + 0.274a_{t-2}$$

with standard deviation of the residuals as $\hat{\sigma}_e = 0.136$, a small improvement over the MA (0,1,2) model and some slight improvement over the original standard deviation (0.147) of the variable logarithms given in Table 6.2.

Model Fitting: Acid Load (Log)

As a first approximation, an MA (0,1,1) was fitted to these data and a trend term was included to determine if it gave rise to any improvement. The Acf of the residuals yielded a chi-square = 22.41 with 28 degrees of freedom ($0.80 > P > 0.70$), not significantly different from an Acf of white noise. A barely significant spike occurred at lag 16 in the Acf and Pacf. It was not supported by any other diagnostic characteristic and so was ignored. The correlation coefficient

between the trend constant and the MA coefficient ($\hat{\theta}_1 = -0.01$). Therefore, they are effectively independent. However, on testing the trend term, its 95% confidence limits include zero, and therefore, the trend constant does not make any real contribution to explaining the variation of log acid load. The MA coefficient ($\hat{\theta}_1 = 0.247$) is real. The equation may be expressed as (the trend term is omitted for reasons given above):

$$z_t = a_t - 0.247a_{t-1}$$

The standard deviation of the residuals is 0.355, which is approximately half the original standard deviation of 0.614.

Two other models were fitted to these data (an ARI (1,1,0) and an ARMA (1,0,1)), again assuming that the AR coefficient would proxy for the first difference in the ARMA model. A chi-square of the residuals from the ARI model yielded 22.11 with 29 degrees of freedom ($0.90 > P > 0.80$). Clearly, the first differences and the autoregressive coefficient ($\hat{\Phi}_1$) reduced any unusual occurrences in the data. There were no significant spikes in the Acf but there is a possible one at lag 16 in the Pacf (i.e. the MA (0,1,1) model). The AR coefficient was significantly different from zero ($\hat{\Phi}_1 = -0.203$) and the standard deviation of the residuals is $\hat{\sigma}_e = 0.353$, a considerable reduction from the original value of 0.614 for standard deviation of the logarithms (see Table 6.2). The equation is:

$$z_t = 0.797z_{t-1} - 0.203z_{t-2} + a_t$$

The ARMA (1,0,1) model possessed two coefficients and a mean. Their respective correlations were $r_{12}(\hat{\Phi}_1 \text{ vs. } \bar{X}) = 0.03$, $r_{13} = 0.55$, and $r_{23}(\bar{X} \text{ vs. } \hat{\theta}_1) = 0.01$, effectively independent for the first and third and not very large for the second. Acf of the residuals yielded a chi-square of 24.32 with 27 degrees of freedom ($0.70 > P > 0.50$), indicating no significant difference from an Acf for white noise. The autoregressive coefficient ($\hat{\Phi}_1 = 0.881$) and the mean ($\bar{X} = 3.196$) were real, whereas the 95% confidence limits around the moving average coefficient ($\hat{\theta}_1 = 0.171$) contains zero. The standard deviation of the residuals is 0.347, the same order of magnitude as the previous models fitted to log acid load.

Summary

It is somewhat surprising that there appears to be no seasonal component in the time series models, particularly in the load variables. The only satisfactory explanation appears to be the existence of too many maxima at too many different times with very little repetition during the same time period.

Most of the variables show the presence of a trend over time (pH, flow, acidity, acid load, iron load, ferrous iron). These variables need a first difference to remove the effects of the trend. It

seems evident from the studies to date that a moving average model applied to the first differences is almost universally the best choice. In some cases, the autoregressive model, possibly with a first difference, is also appropriate. In both cases, there is an indicator that the variation in whichever parameter is being analyzed, when first differenced, leads to a random walk.

The quality control analysis, in both cases, suggests that either the mean (plus or minus two standard deviations) or the non-parametric median (plus or minus a function of the H-spread) are equally appropriate. For the present, it is recommended both should be used until one or the other show superior performance.

Chapter 7: Analysis of Data from the Fisher Deep Mine Site, Lycoming County, PA

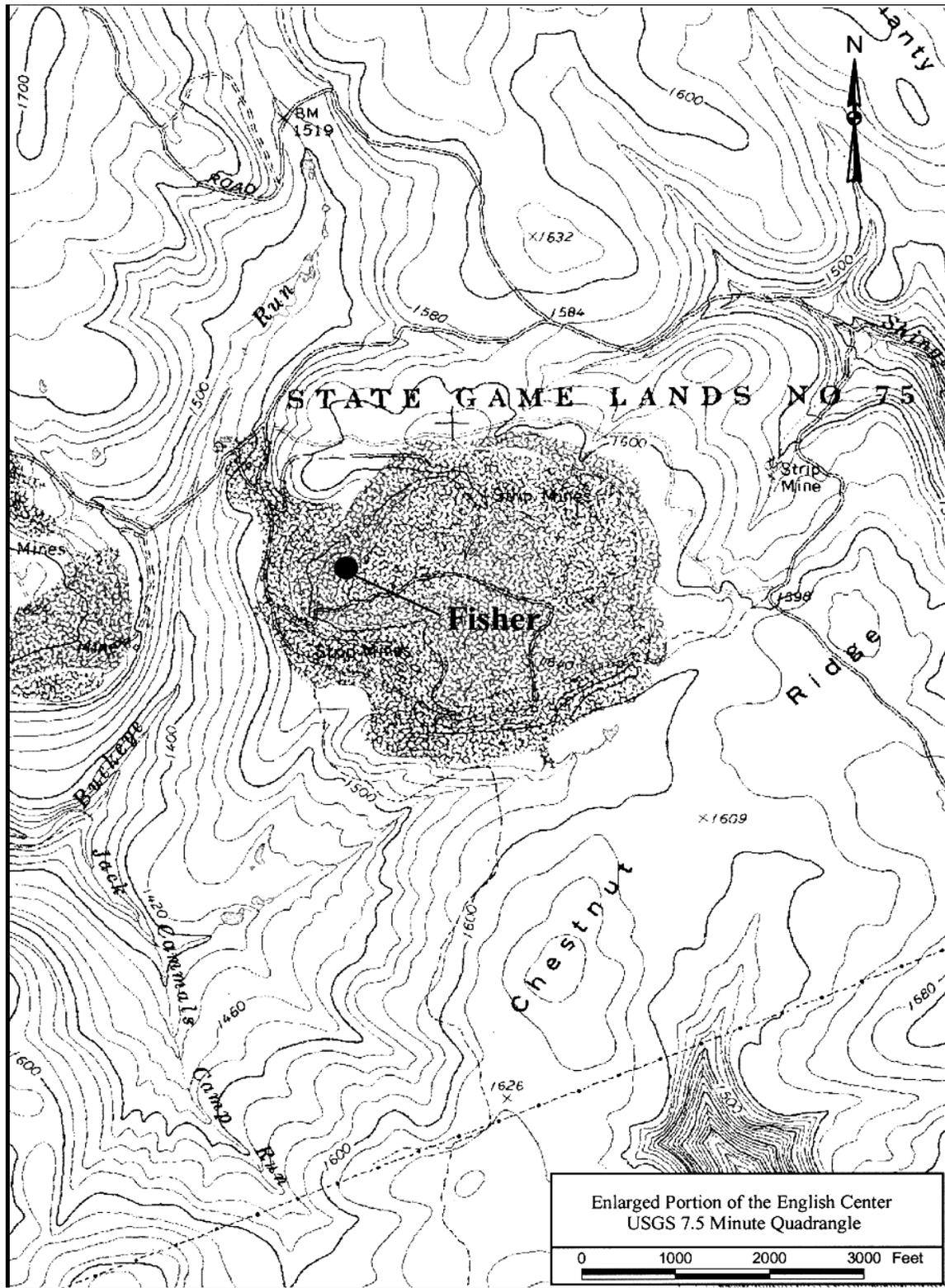
The Fisher site is located in Lycoming County, Pennsylvania near the village of English Center (Figure 7.0). Prior to remining on this site, the land surface was extensively disturbed by abandoned mine pits and spoil piles, and the Fisher deep mine, a large abandoned underground mine, occupied much of the subsurface. Fisher deep mine discharge (monitoring point M-1) characteristics have been discussed in numerous other reports including Section 5 of EPA's *Coal Remining Statistical Support Document* (EPA-821-B-00-001).

The Fisher deep mine discharge and its impact on the receiving streams is discussed in an Operation Scarlift Report of 1977 on the Little Pine Creek Watershed. The Buckeye Run and Otter Run tributaries of the Little Pine Creek were impacted by AMD from the Fisher deep mine. Otter Run was a prolific native brook trout stream prior to being impacted by the Fisher deep mine discharge, and it has returned to a trout fishery as the result of remining operations. Descriptions of the remining operation, geologic characteristics of the area and water quality improvements are included in Plowman (1989) and Smith and Dodge (1995).

The data set that was analyzed statistically in this chapter (see report by Dr. J.C. Griffiths, December 1987) includes all baseline pollution load data (i.e., prior to issuance of the first remining permit) and data from the first year and a half of remining. Baseline pollution load data collection took place from May/June 1982 through 1985. The primary remining permit was issued on November 5, 1985, and remining operations commenced by February 1986. Final coal removal occurred on June 1995 and backfilling was essentially completed within that permit area by February 1996. The primary remining permit for this site is contiguous to a previous permit that did not involve daylighting and to a subsequent remining permit that was issued in 1994 and completed in July 1999 (that also drained to the M-1 discharge). The total acreage of these three permits is 542, of which approximately 200 acres were mined under the initial permit (issued prior to 1985). The data set included in Section 5 of the EPA *Coal Remining Statistical Support Document* includes monitoring data for the M-1 discharge from 1981 to 1998. Time plots and box plots of net acidity, acid load, iron load and net alkalinity show changes in water quality and pollution load over the four year baseline period, ten years of remining, and two years following the completion of backfilling of the remining site.

The data analysis presented in this chapter follows the usual flow diagram (Figure 3.1). The data consist of 79 observations of seven parameters. Flow measurements began on June 9, 1982 and remining of the site began on February 4, 1986. There were three observations prior to June 9, 1982 (see Appendix E Table). After excluding these observations and inserting mean values for samples with a missing parameter, 57 observations remained prior to remining and 19 observations remained after remining commenced. From the histograms showing skewness of varying degrees, it was decided to log-transform (base ten) the data.

Figure 7.0: Map of Fisher Mine Site



After preliminary analysis of the data, the bivariate and time series plots appeared to be somewhat irregular, and it was decided to measure the intervals between the observations by creating a new variable (the first differences between the number of days).

The intervals between observations (days) vary from extremes of one to 104, with a mean of 26.7 days. This mean is nearly equal to the median (26.5), indicating that the frequency distribution is symmetrical. The central part of the distribution Q_1 to Q_3 lies between 12.7 and 33 days. The most serious discrepancies are, however, that there are five observations between 70 and 104 days, and four of these are 90 days or more. These large gaps in the data preclude rigorous time series analysis which requires approximately equal intervals between observations.

Univariate Analysis

The coefficient of variation (CV%) for flow, acidity, sulfate and manganese (Table 7.1) are all less than or equal to 20%. This is surprisingly low when compared to previous data analysis. Iron, however, possesses a coefficient of variation of 929 % and aluminum also has a large CV (71%).

Table 7.1: Summary Statistics for 79 Log Transformed Observations

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Flow	79	0	1.7882	1.8062	1.7754	0.3734	0.0420
Acidity	79	0	1.8700	1.8274	1.8660	0.2183	0.0246
SO ₄	79	0	2.5316	2.5105	2.5342	0.2124	0.0239
Total Iron	79	0	0.0442	0.0825	0.0575	0.4106	0.0462
Mn	79	0	0.9396	0.9513	0.9335	0.1716	0.0193
Al	79	0	0.4959	0.5539	0.5029	0.3539	0.0398
Interval	78	1	26.72	26.50	24.20	19.95	2.26

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Flow	0.9542	2.7882	1.4771	2.0000	20.9
Acidity	1.4409	2.3747	1.7076	2.0453	11.7
SO ₄	1.6902	3.0792	2.4346	2.6335	8.4
Total Iron	-1.301	0.8450	-0.1024	0.2032	929.3
Mn	0.5775	1.5185	0.8500	1.0253	18.3
Al	-0.4948	1.4698	0.3598	0.6628	71.4
Interval	1.00	104.00	12.75	33.00	

There is little doubt that the coefficient of variation for iron is misleading and serves to illustrate one of the dangers of using the CV%. When the mean is very small, as in this case, the CV tends to become very large, particularly in ratio-type data (i.e., percent or concentration, Griffiths, 1967, Chapter 15, page 316). It should be used on log data with great care, if at all.

When the data are subdivided into 57 observations (from the beginning of flow measurement to immediately prior to remining, Table 7.2a), and into 19 observations (after commencement of remining, Table 7.2b), the CVs of flow, acidity, sulfate, and manganese remain substantially similar. Iron, however, shows a marked drop from a CV equal to 109.2 % to a CV equal to 50.2%, implying that there was a major change in variability after the start of remining. The CV of aluminum, on the other hand, shows no change from the original data set.

Table 7.2a: Summary Statistics for 57 Log Transformed Observations (Pre-remining)

	N	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Flow	57	1.7885	1.8062	1.7751	0.3793	0.0502
Acidity	57	1.9176	1.9222	1.9170	0.1964	0.0260
SO₄	57	2.4654	2.4771	2.4744	0.1881	0.0249
Total Iron	57	0.2027	0.1461	0.1961	0.2214	0.0293
Mn	57	0.9661	0.9713	0.9652	0.1302	0.0172
Al	57	0.4874	0.5250	0.4928	0.3520	0.0466

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Flow	0.9542	2.7882	1.4771	2.000	21.2
Acidity	1.4564	2.3747	1.7489	2.0737	10.2
SO₄	1.6902	3.0792	2.4013	2.5682	7.6
Total Iron	-0.1427	0.7243	0.0453	0.3444	109.2
Mn	0.5775	1.4048	0.8836	1.0528	13.5
Al	-0.4948	1.4698	0.3874	0.6389	72.2

Table 7.2b: Summary Statistics for 19 Log Transformed Observations (During remining)

	N	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Flow	19	1.7702	1.8062	1.7551	0.3867	0.0887
Acidity	19	1.6673	1.6928	1.6733	0.1018	0.0234
SO₄	19	2.6844	2.6335	2.6830	0.1695	0.0389
Total Iron	19	-0.5345	-0.5376	-0.5170	0.2684	0.0616
Mn	19	0.7988	0.7672	0.7953	0.1430	0.0328
Al	19	0.4865	0.6542	0.4954	0.3818	0.0876

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Flow	1.1461	2.6513	1.4771	2.0000	21.8
Acidity	1.4409	1.7924	1.5694	1.7543	6.1
SO₄	2.4150	2.9777	2.5658	2.8751	6.3
Total Iron	-1.3010	-0.0655	-0.6021	-0.3565	50.2
Mn	0.6010	1.0569	0.6656	0.9101	17.9
Al	-0.3010	1.1239	0.2504	0.7627	78.5

The means also show interesting changes. Acidity possesses an overall mean of 1.87. In comparison, the mean of acidity prior to remining (1.92) is larger than during remining (e.g., see Figure 2.5, Chapter 2). Sulfate is lower than the overall mean prior to remining and much higher than the overall mean during remining. Log iron shows the most substantial change, from 0.20 before remining (approximately 1.6 in untransformed data units) to -0.53 (0.295) after after remining operations began. This represents a very large and favorable change because the pollution load has been reduced. Manganese also shows a quite large change from before to during remining.

The histograms of log transformed flow (Figure 7.1a), acidity (Figure 7.1b), iron (Figure 7.1c), manganese (Figure 7.1d), and aluminum (Figure 7.1e) are essentially symmetrical, thus the transformation has sufficed to reduce the asymmetry in the original data. Because of the gaps in the data and their peculiar pattern of variation, it was decided to graph some of the parameters to show the distribution of gaps and to examine the pattern for cycles.

Figure 7.1a: Histogram of Log Flow

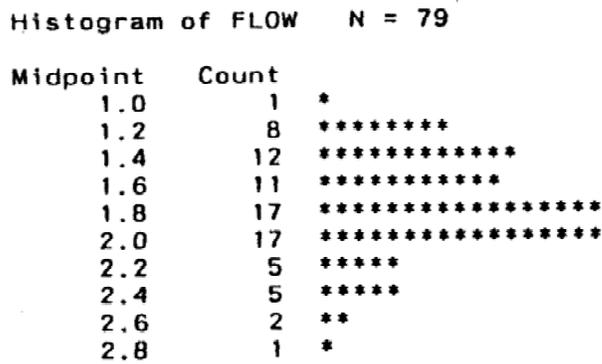


Figure 7.1b: Histogram of Log Acid

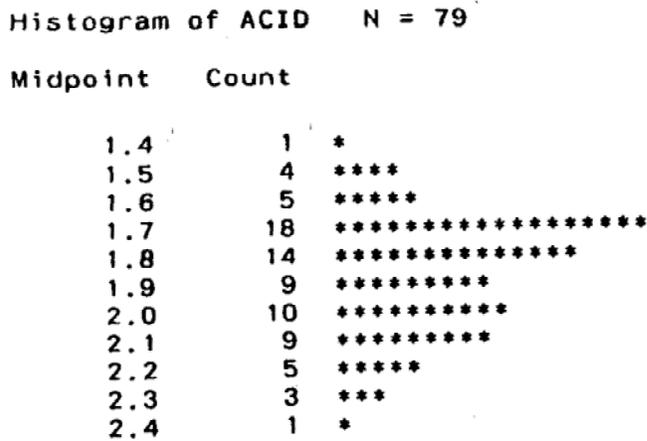


Figure 7.1c: Histogram of Log Iron

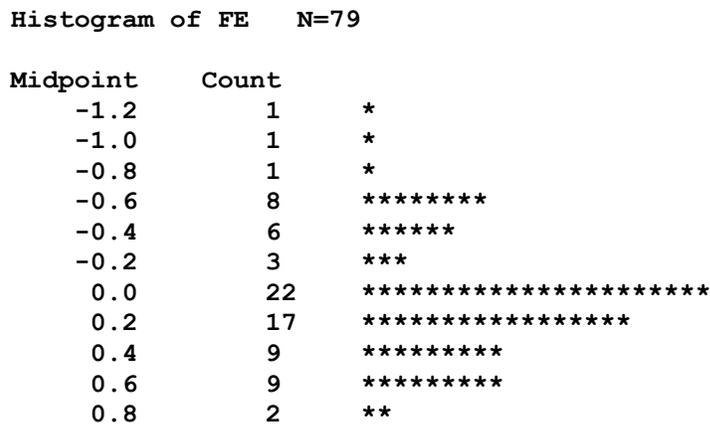


Figure 7.1d: Histogram of Log Manganese

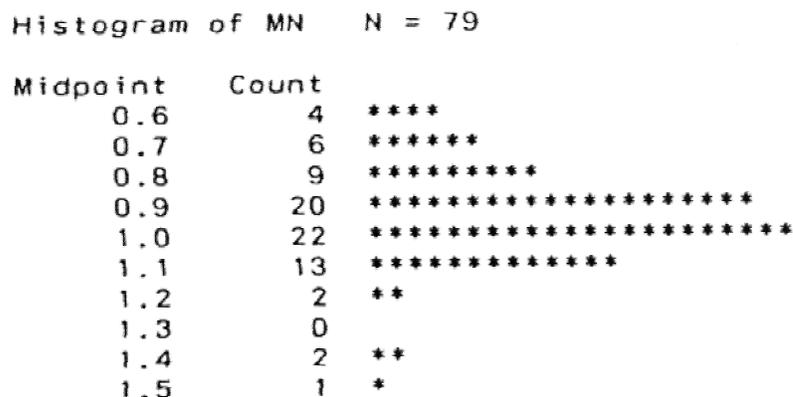
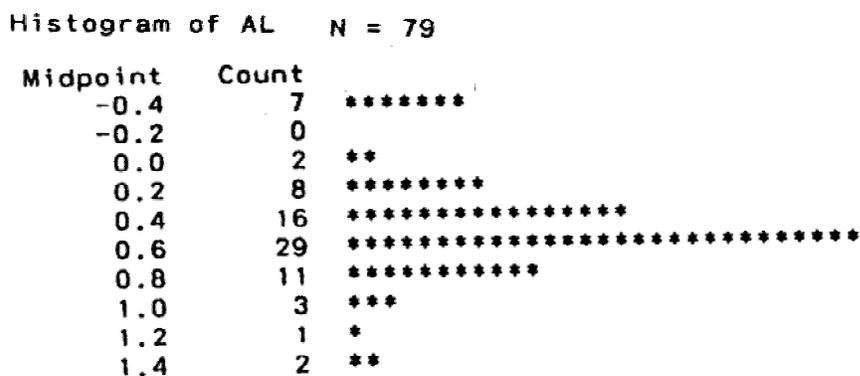


Figure 7.1e: Histogram of Log Aluminum



Log flow versus days is shown in Figure 7.2a, and there does not appear to be much change coincident with the start of remining. Furthermore, peak flows occur in various months throughout the record; there are two in June (1982, 1985) and two in April (1984, 1987) for example, but they do not appear to recur each year. No persistent cyclic pattern is evident for flow.

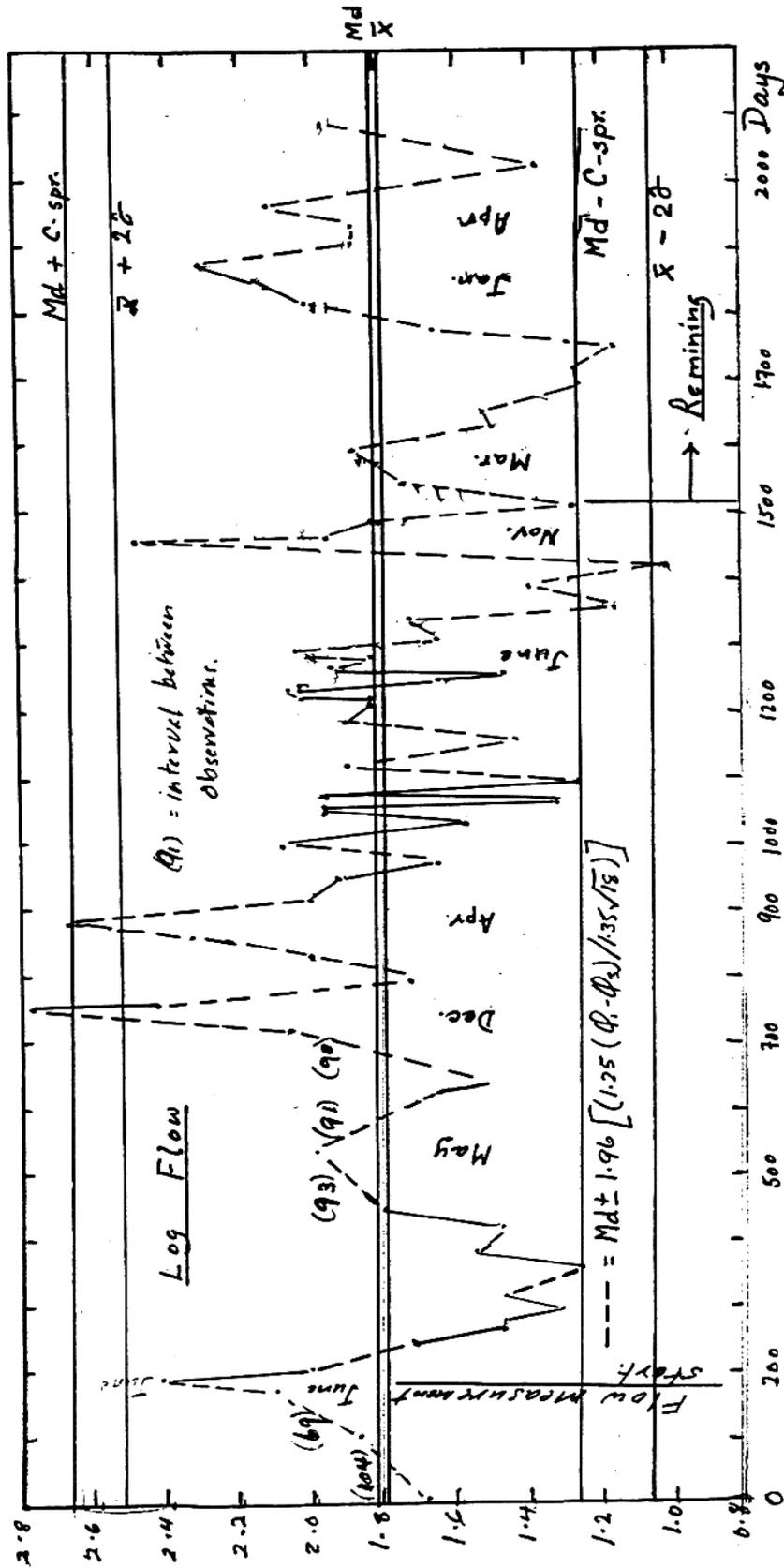
Log acidity (Figure 7.2b) shows a large change, remaining well above both the mean and median from November 27, 1981 to September 6, 1984, then falling to the mean around December 18, 1984 and falling consistently below both mean and median following October 26, 1985. This change took place prior to activation of the remining permit. However, mining was occurring on an adjacent surface mine prior to 1985. The mean prior to remining (N = 57, Table 7.2a), is 1.9176 (log transformed) and is 82.7 in untransformed units. After remining, the mean is 1.6673 in log-transformed units and 46.5 in untransformed units. When the quality control limits around

the median are inserted using a sample size of 18, the post-remining median is significantly below the pre-remining limits (see lines in Figure 7.2b).

Graphs of log iron and log manganese are included in Figures 7.2c and 7.2d respectively. Log iron shows a marked decrease over time during the pre-remining period with a sharp decline immediately following commencement of remining. The confidence limits around the median of pre-remining are inserted in the graph. The median and the confidence limits, after remining began, are much lower and the median lies outside the confidence limits of pre-mining.

Log manganese also shows a decrease after remining began but is not nearly so marked as is log iron. However, as in the case of log iron, the median log manganese after remining remains outside (below) the pre-remining confidence limits. Log aluminum is plotted against days (Figure 7.2e), and the pre- and post-remining statistics are fairly similar. The post-remining median lies within the confidence limits (for $N^* = 18$) of the pre-remining performance. There is no substantial change in the central tendency.

Figure 7.2a: Log Flow vs. Time (Days)



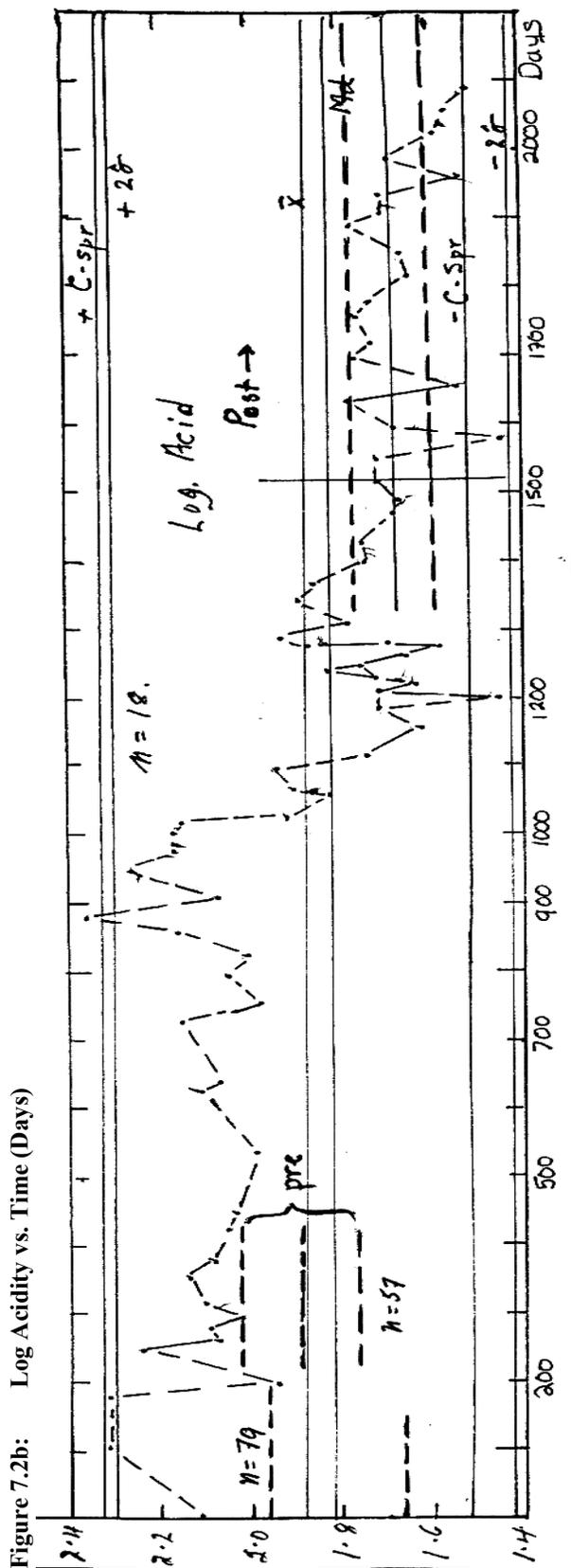


Figure 7.2c: Log Iron vs. Time (Days)

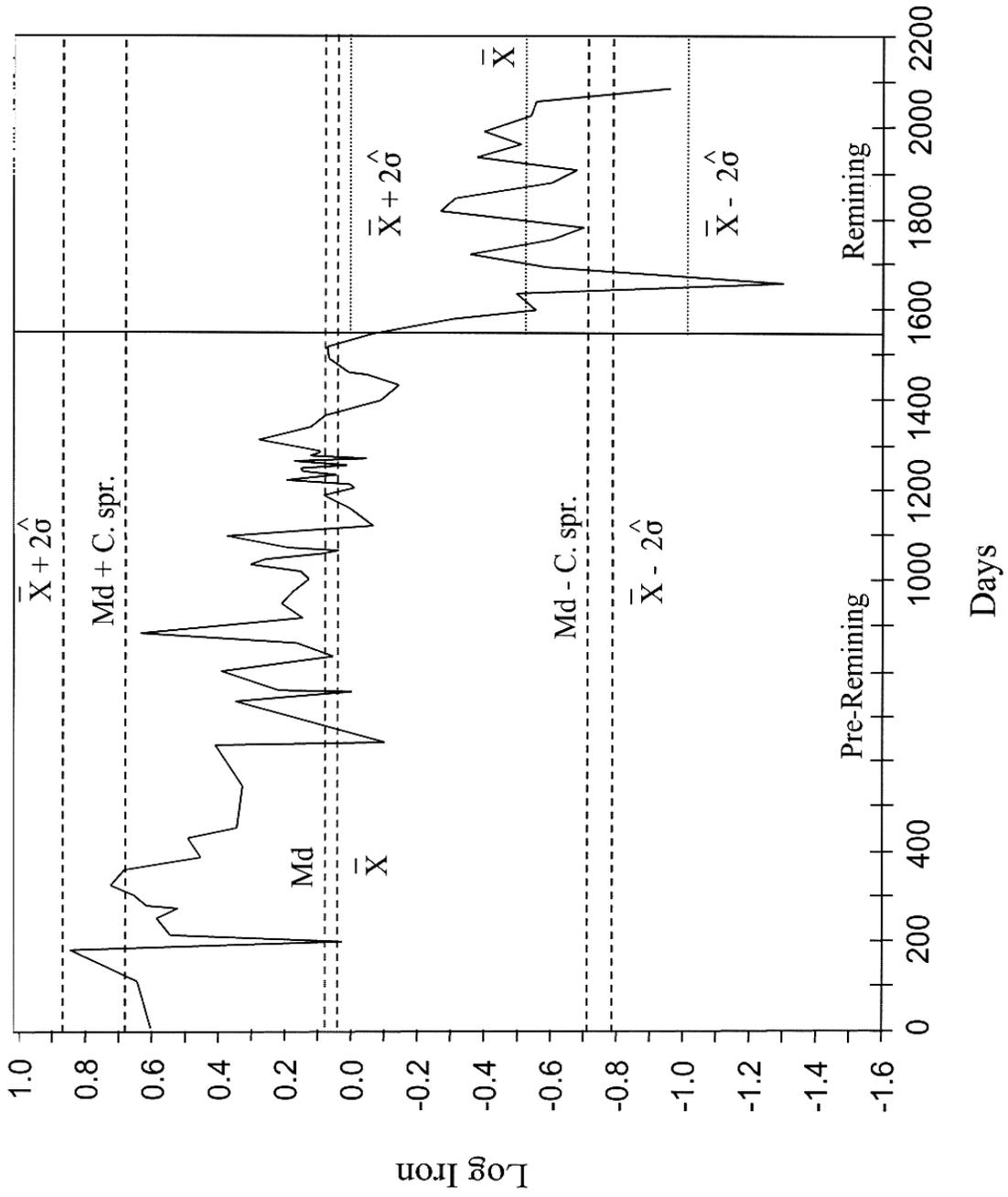
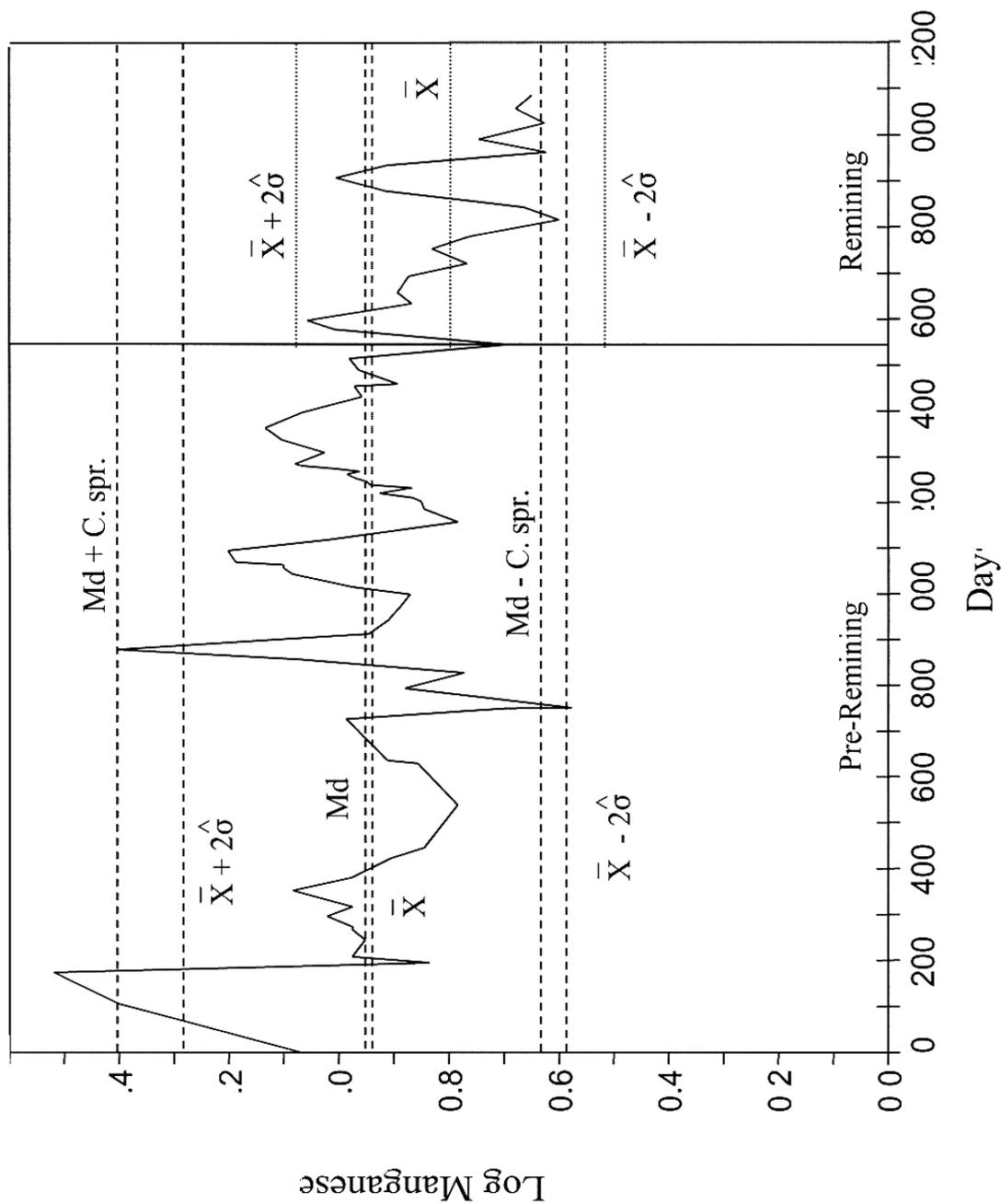
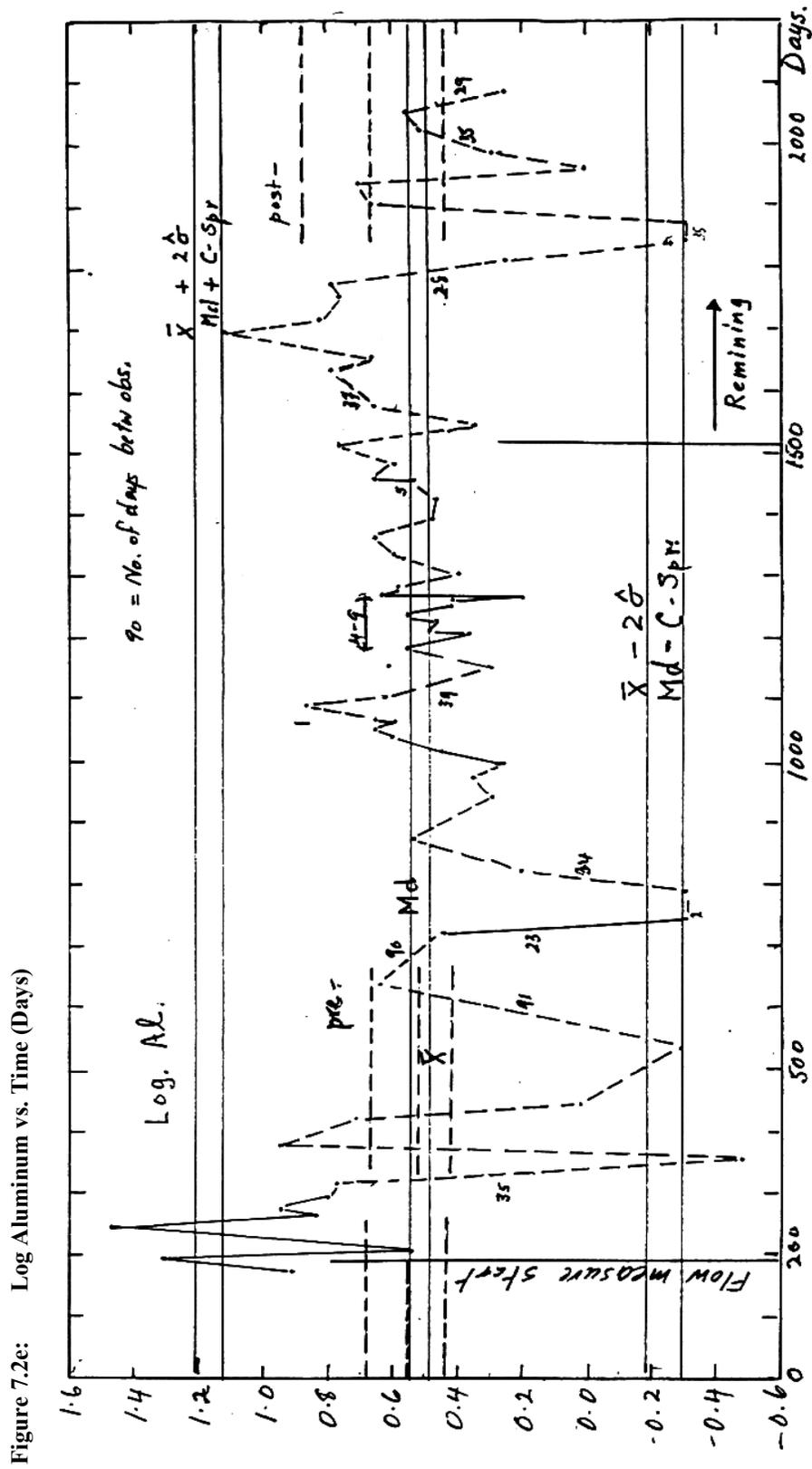


Figure 7.2d: Log Manganese vs. Time (Days)





Another comparison of interest between pre- and post-remining water quality concerns variances, and parameter pairs may be compared by a variance ratio or F-test. It is customary to divide the smaller variance into the larger so that the outcome always equals or exceeds one. This is in accord with the F-table of values which tests only that half of the F distribution that exceeds unity. In this case, it begins with the flow variables as follows: the calculated ratio, $F_{\text{calc}} = 0.1495/0.1439 = 1.039$. The expected F-value ($F_{18,55} = 1.79$, at the five percent level) is much larger, thus, there is no difference in the variances before and after remining.

In the variance ratio for acidity, F_{calc} equals $0.0386/0.0104 = 3.722$. The five percent level of expected F for these degrees of freedom (df) is $F_{50,18} = 2.02$, so that the variance for pre-remining is significantly larger than that for post-remining (a desirable outcome). The same test performed for SO_4 yields F_{calc} equal to $0.0354/0.0287 = 1.232$. Thus, the pre-remining variance is not significantly different from that after remining.

For iron, F_{calc} equals $0.0720/0.0490 = 1.469$ (not significantly greater than a 5% probability level of $F_{18,56} = 1.79$). The variance of iron concentration after remining is not significantly different from the variance of iron concentration before remining. Manganese has a slightly larger variance post- than pre-remining yielding an $F_{\text{calc}} = 0.020/0.017 = 1.206$, but the difference in variability is not statistically significant. Aluminum also possesses a larger variance after remining than before; the corresponding $F_{\text{calc}} = 0.1458/0.1239 = 1.176$. This difference is not significant.

The behavior of the variance before and after the beginning of remining is as important as the differences in mean or median. This is because if the variance becomes significantly smaller after remining begins, the observed value is much less likely to exceed the confidence limits at some future time, assuming that the behavior remains consistent.

Bivariate Analysis

Examination of the relationship among pairs of variables begins with the correlations of zero order among all pairs of the seven variables (Table 7.3). The expected value of the correlation coefficient for a pair of variables with 79 observations (= 78 df), each taken from a population in which there is no correlation, is approximately $r = 0.217$ (using 80 df from Table 21, Arkin and Colton, 1950, p. 140, Table of r for the 1% and 5% points of the r distribution). This means that any $r < 0.217$ is not significantly different from zero. This value is found at the top of Table 7.3.

Table 7.3: Correlations of Zero Order Among the Seven Variables

Correlation of Seven Variables						
	Days	Flow	Acidity	SO ₄	Total Iron	Mn
Flow	-0.044					
Acidity	-0.783	0.082				
SO ₄	0.199	-0.006	-0.093			
Total Iron	-0.852	-0.013	0.724	-0.211		
Mn	-0.410	-0.042	0.457	0.396	0.510	
Al	-0.121	-0.307	0.058	0.250	0.055	0.361

Pairing each variable in turn, against days, shows that a linear association between flow, sulfate, or aluminum and days is unlikely. The relationship between acidity and days is negative (i.e., inverse). Acidity decreases as days increase. This is also the case with the relationship between days and iron. In both cases, the proportion of common association (r) among the pairs of variables is large, 61% for acidity and 73% for iron. Manganese also shows an inverse relationship with days but the degree of association is much less ($r^2 = 17\%$).

Relationships between flow and the other variables, as measured by the correlation coefficient, is effectively zero. The exception is aluminum, where the relationship is negative (inverse) and the degree of association is not very strong ($r^2 = 9\%$).

Acidity appears to have no simple linear relationship with either sulfate or aluminum, however, it is positively associated with iron, possessing an $r^2 = 52\%$ in common. Acidity has $r^2 = 21\%$ common association with manganese and again the relationship is positive (i.e., they increase or decrease together). Sulfate and manganese are positively associated but the degree of common association is weak. Variation in manganese is related to variation in iron in the same way but to a slightly greater degree. Manganese is also weakly positively associated with aluminum (the degree of common association $r^2 = 13\%$). The strongest correlation coefficient values are between the pairs of acidity and days, and iron and days. The decline of acidity and iron with time is obvious in Figures 7.2b and 7.2c. It is no surprise, therefore, that the third strongest association is the positive one between iron and acidity.

As a check that perhaps the maximum degree of association was not of zero order, the cross-correlation functions (CCF) were run and the principal outcomes are listed in Table 7.4. To evaluate these functions, it is reasonable to take a conservative value (for example, $r = 0.3$) as the limit below which the relationship is not significantly different from zero. In the case of flow versus the other variables, there appears to be no linear association except for aluminum which has its highest value as inverse (-0.389) at lag -4 . It is likely that the zero order value of -0.302 is not really significantly different from the r value at lag -4 .

Table 7.4: Summary of Important Cross-correlation Functions (CCF) Among Seven Variables

	Variables	r_{\max}	lag @ r_{\max}	$ r > 0.3$
1.	Flow vs. Acid	0.248	- 16	none
2.	Flow vs. SO ₄	- 0.254	- 4	none
3.	Flow vs. Fe	0.214	10	none
4.	Flow vs. Mn	- 0.276	- 4	none
5.	Flow vs. Al	- 0.389	- 4	-4, -3, 0
6.	Acid vs. SO ₄	- 0.367	14	2 to 4, 14, 15
7.	Acid vs. Fe	0.724	0	- 14 to 14, 16 to 18
8.	Acid vs. Mn	0.457	0	0, 1
9.	Acid vs. Al	0.252	- 18	none
10.	SO ₄ vs. Fe	- 0.361	-7	- 9 to - 6, - 4, 2
11.	SO ₄ vs. Mn	0.396	0	0, 3 to 5
12.	SO ₄ vs. Al	0.299	1	none
13.	Fe vs. Mn	0.511	0	-2 to 3
14.	Fe vs. Al	- 0.188	- 12	none
15.	Mn vs. Al	0.441	1	- 13, 0, 1
16.	Acidity vs. days	- 0.783	0	- 18 to 17
17.	Iron vs days	- 0.852	0	-17, - 15 to 13

Acidity versus sulfate, iron, and manganese are all larger than the critical value of 0.3. The cross-correlation function for sulfate has three values exceeding 0.3 (at lags of +4, +2 and +14). However, these values are all indicative of a low degree of association (<13%) between the two variables. Iron and manganese achieve their maximum r at zero lag.

Sulfate versus iron, manganese, and aluminum show correlations between 0.3 (0.299) and 0.396. These values are all significantly different from zero. Correlations are positive between sulfate, manganese, and aluminum, but negative with iron. Sulfate behaves independently in all associations with other variables. The maximum correlation between iron and manganese (0.510) occurred at 0 lag, and indicates a relatively strong degree of association (26%). The relationship between iron and aluminum never exceeded the critical value of $r = 0.217$.

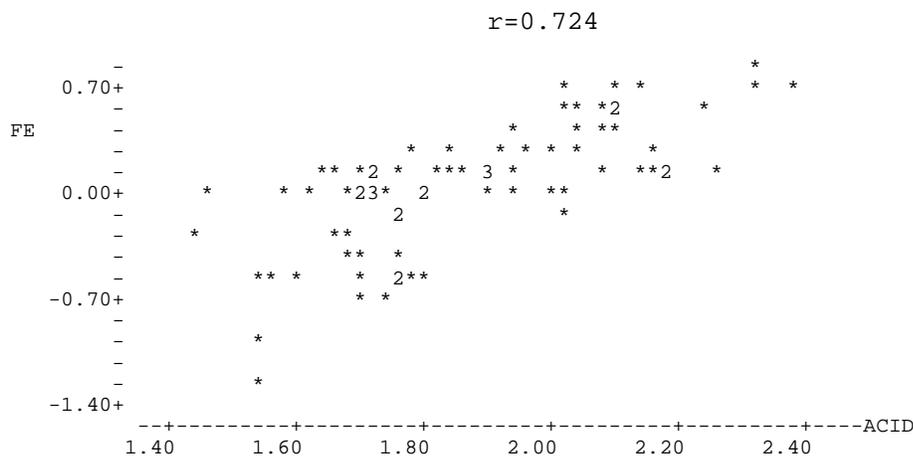
The correlation between iron and manganese is very weak (<26%) and the maximum is at zero lag. The relationship between iron and aluminum does not exceed the critical value of 0.217 (see Table 7.3).

The relationship of manganese and aluminum exceeds the critical value of 0.217 at lag -13 to -10, lag 0 to 1, and lag 17. The maximum r (0.441) occurs at lag 1. Again, if this is a real association, it is weak ($r^2 = 19\%$).

Bivariate relationships between pairs of water quality parameters and flow vs. water quality parameters were plotted. The results yielded very little that was meaningful with the exception of iron vs. acidity (Figure 7.3). This relationship had the highest positive correlation coefficient ($r = 0.724$).

Figure 7.3: Plot of Log Iron vs. Acidity

MTB > PLOT C5 VS C3



Time Series Analysis

This analysis is subdivided into three parts. First, there is a plot of each variable versus the date collected. The dates are forced into 79 equal intervals, distorting the graph in terms of horizontal scale. (The correct spacing may be seen in Figures 7.2a to 7.2d.) The second subdivision details the diagnosis phase of the Box-Jenkins time series analysis using the autocorrelation and partial autocorrelation functions (Acf and Pacf, respectively). The third stage comprises modeling using Box-Jenkins estimation and forecasting programs.

The time series graphs begin with a plot using the variable of the first differences between collection dates against the observation number(s) (Figure 7.4a). The trend increases consistently through time. Figure 7.4a is included as an example of what happens when a variable of known structure is analyzed, where any variable with a constant function (increasing or decreasing) over time will yield a typical Acf and Pacf (Figures 7.5a and 7.5b).

Log flow is plotted against equal intervals in Figure 7.4b. The variation around the mean appears to remain reasonably constant throughout the period of observation. By contrast, in a plot of log acidity versus date (Figure 7.4c) the variation in acidity is consistently high and above

the mean until approximately the 29th observation (September 6, 1984), when it decreases to the mean from observation 30 to 36 (September 21, 1984 to November 23, 1984). The pattern of variation then falls well below the mean from observation 37 to 49 (December 18, 1984 to May 22, 1985); from observation 50 to 54 (May 28, 1985 to August 19, 1985) it remains close to the mean, and from 55 to 79 (September 21, 1985 to August 12, 1987) the range of acidity values remains consistently below the mean. Remining began at observation 61 (February 17, 1986).

Sulfate versus observation number (Figure 7.4d) shows no substantive change in variation around the mean throughout all 79 observations. The plot of iron versus observation number (Figure 7.4e) shows a slight decreasing trend prior to remining at observation 61. From observation 62 (March 22, 1986) onwards, the variation is well below the mean with two observations (65, June 10, 1986 and 89, August 12, 1987) below the lower two standard deviation limit.

Fluctuations in the concentrations of manganese (Figure 7.4f) are quite large, particularly in the beginning (observations 1 through 3, November 27, 1981 to May 19, 1982). From observation 4 through observation 66 (June 9, 1982 through July 15, 1986), the fluctuations are around the mean (= the median), and from observation 67 to 79 (August 12, 1986 to August 12, 1987), the observations tend to fall below the mean, varying widely, from observation 73 (February 14, 1987) slightly above the mean to observation 70 and observations 75 to 79 (November 15, 1986 and April 11, 1987 to August 12, 1987) near the lower confidence limits.

The time series plot of aluminum (Figure 7.4g) begins well above the mean (= the median) in observations 3 to 9 (May 19, 1982 to September 18, 1982), then falls well below the mean for observations 11 to 22 (November 13, 1982 to March 2, 1984). Observations 11, 15, and 19 to 21 (November 13, 1982, May 18, 1983 and December 15, 1983 to January 28, 1984) are all below the lower confidence limits. For observations 23 to 79 (March 31, 1984 to August 12, 1987), the concentration falls around the mean with two strong deviations to the lower confidence limits at observations 71 and 72 (December 13, 1986 and January 17, 1987). Remining does not seem to have had any consistent effect.

Figure 7.4c: Plot of Log Acidity vs. Time

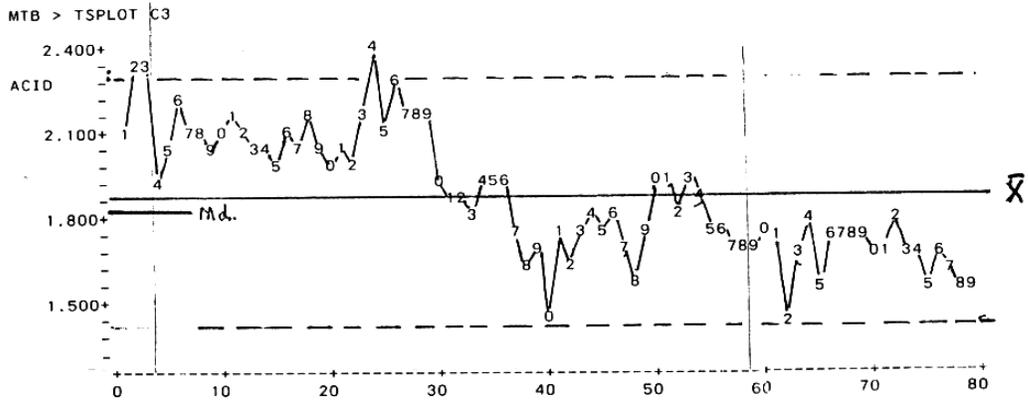


Figure 7.4d: Plot of Log Sulfate vs. Time

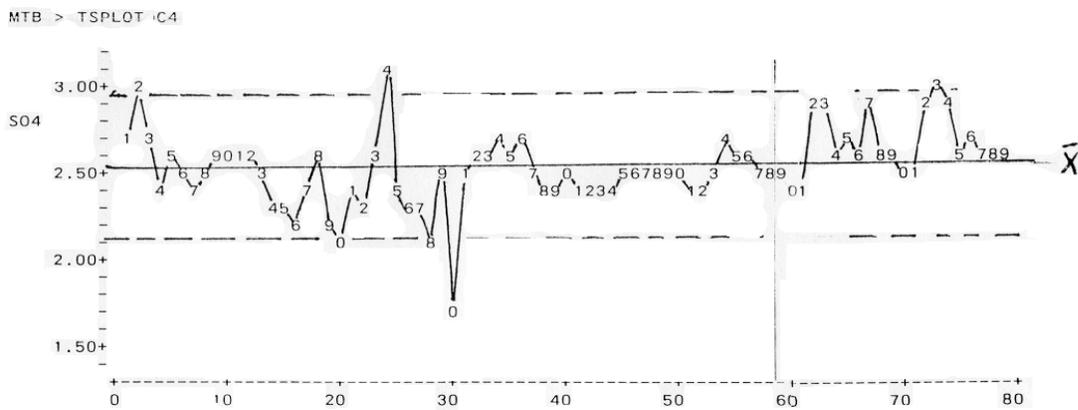


Figure 7.4e: Plot of Log Iron vs. Time

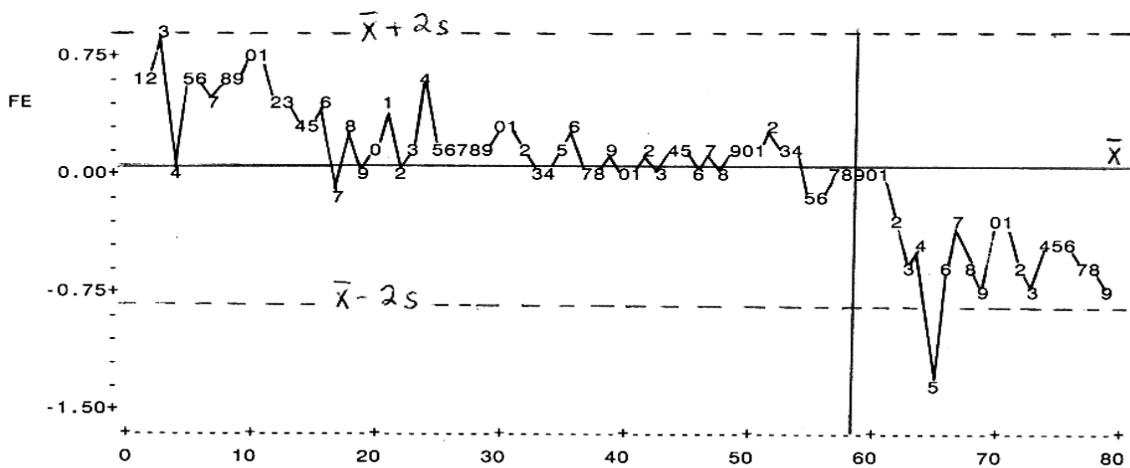


Figure 7.4f: Plot of Log Manganese vs. Time

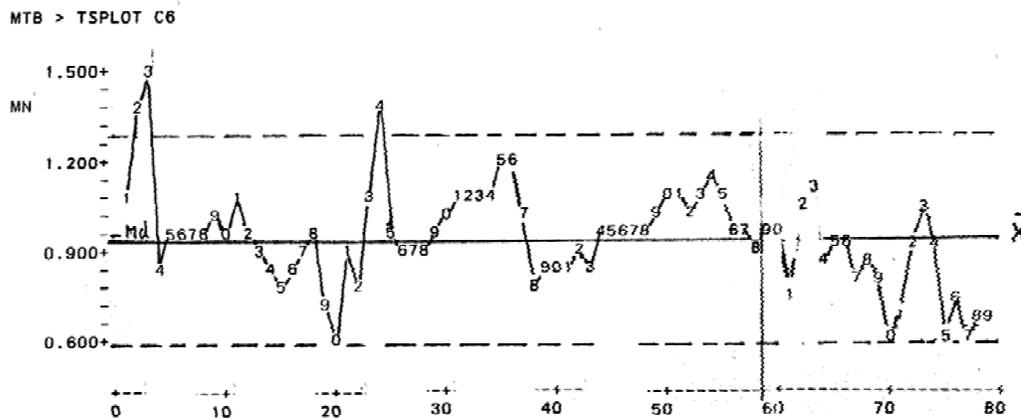
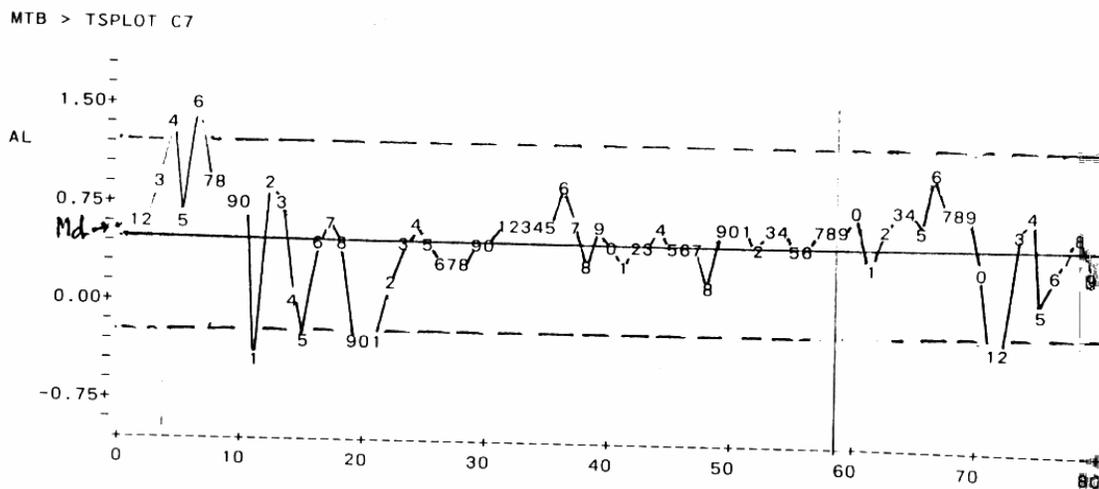


Figure 7.4g: Plot of Log Aluminum vs. Time



Diagnosis of Time Series Models Using Autocorrelation and Partial Autocorrelation Functions

The Acf of days or dates of observation numbers 1 through 79 (Figure 7.5a), shows a steep but uniform decline as would be expected from the consistent increase (i.e., a strong trend) present in Figure 7.4a. The corresponding Pacf (Figure 7.5b) has one large spike at lag 1. The first difference is likely to be a random walk.

The Acf of flow has no distinct patterns, with a single small spike at lag 1 (Figure 7.5c). The Pacf is similar to the Acf (Figure 7.5d), and a simple auto regression (AR(1)) or moving average (MA(1)) model would do equally well (or poorly) in describing the behavior. Acidity, on the

other hand, shows a marked decline in the Acf (Figure 7.5e) similar to that in Figure 7.5a, but somewhat less uniform. The Pacf (Figure 7.5f) has one large spike at lag 1. Here, a first difference is necessary to reduce the variation to a stationary series. Then a simple AR or MA would probably suffice. The Acf and Pacf of sulfate are very similar (Figures 7.5g and 7.5h, respectively), and resemble the corresponding graphs of flow (Figures 7.5c and 7.5d). A small spike at lag 1 and a few subdued features are not likely to be significant.

Iron shows an exponential decline in Acf (Figure 7.5i). The Pacf has a large spike at lag 1, indicating there is a trend over time which should be removed before the series becomes approximately stationary (as shown in Figure 7.5j). The other features appear to be overwhelmed by the trend.

The Acf and Pacf of variation in concentration of log manganese (Figures 7.5k and 7.5l) show similar, if slightly less distinct, characteristics as log Fe concentration. Their variations, in overall terms, are somewhat similar. Again a large spike at lag 1 requires a first difference, but the remainder of the variation is probably not significant. The variation in Acf and Pacf of aluminum (Figures 7.5m and 7.5n) are very similar to each other and to sulfate. Modeling should begin with a simple AR(1) or MA(1) and the complexity should be increased if there are any spikes which are significantly above background.

It appears evident that there are two types of variables in terms of their variation patterns. The first type is very like the first differences (e.g., Figure 7.5a) in possessing a strong trend, not always uniformly decreasing; but acidity, iron and possibly manganese all decrease over time. The second type (e.g., flow, sulfate, and aluminum) shows no well-marked trend but is much more irregular in behavior. When the trend is removed, residual variation will possibly be similar in all six variables.

Figure 7.5a: Autocorrelation Function of Days

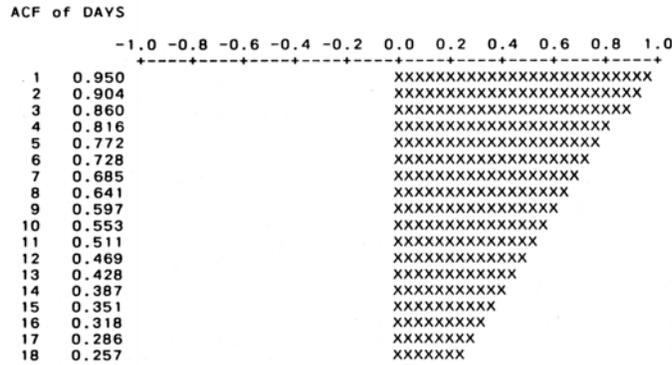


Figure 7.5b: Partial Autocorrelation Function of Days

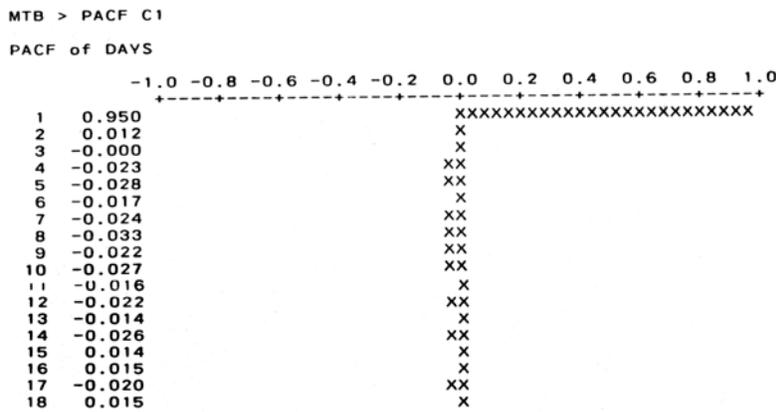


Figure 7.5c: Autocorrelation Function of Flow

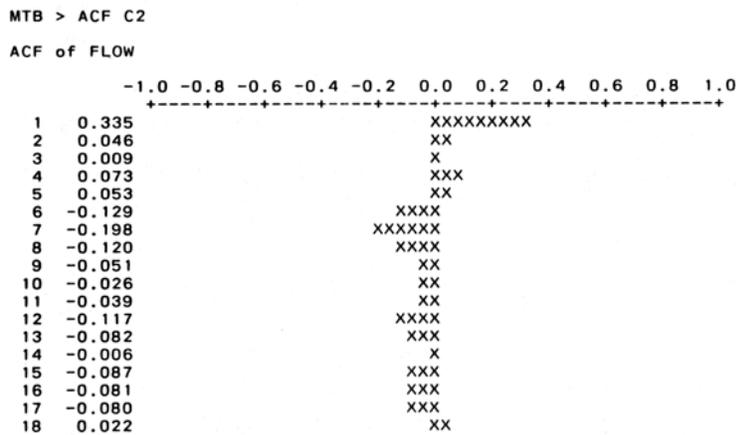


Figure 7.5d: Partial Autocorrelation Function of Flow

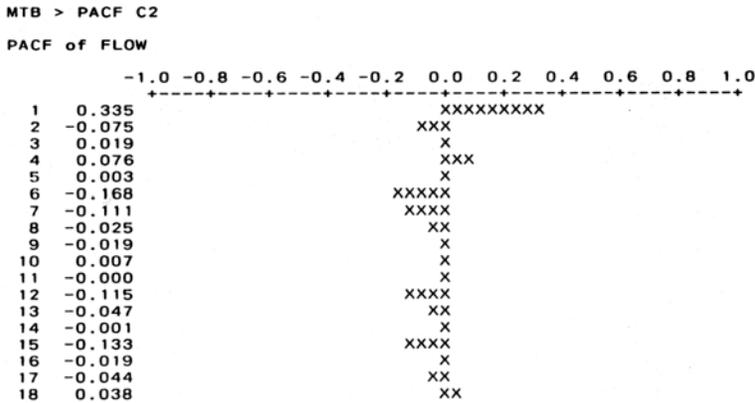


Figure 7.5e: Autocorrelation Function of Acid

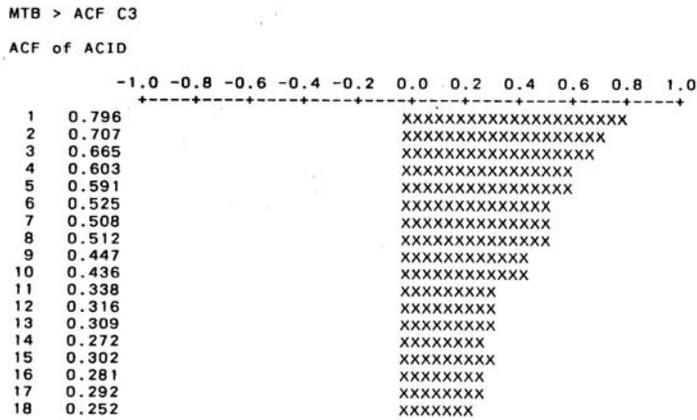


Figure 7.5f: Partial Autocorrelation Function of Acid

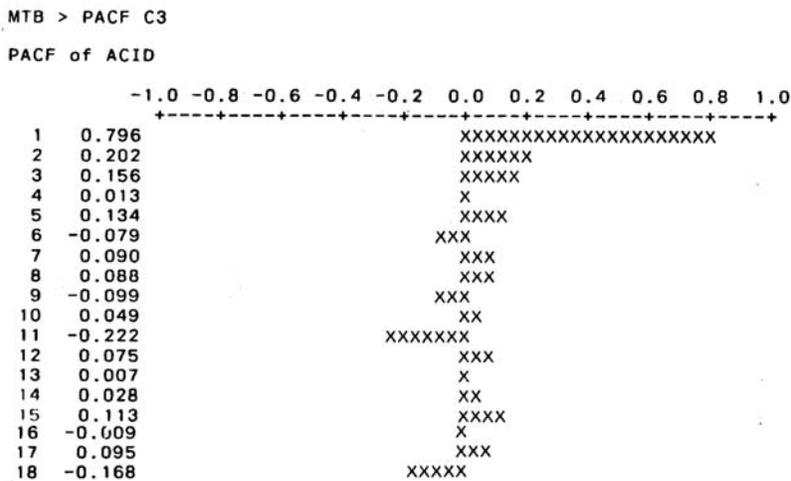


Figure 7.5g: Autocorrelation Function of Sulfate

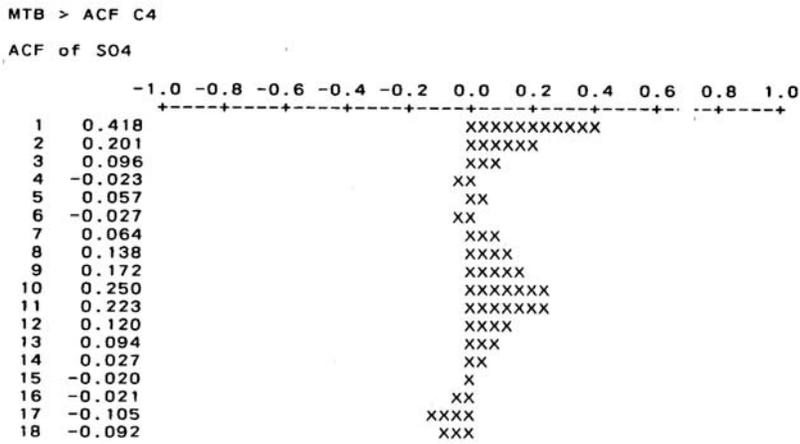


Figure 7.5h: Partial Autocorrelation Function of Sulfate

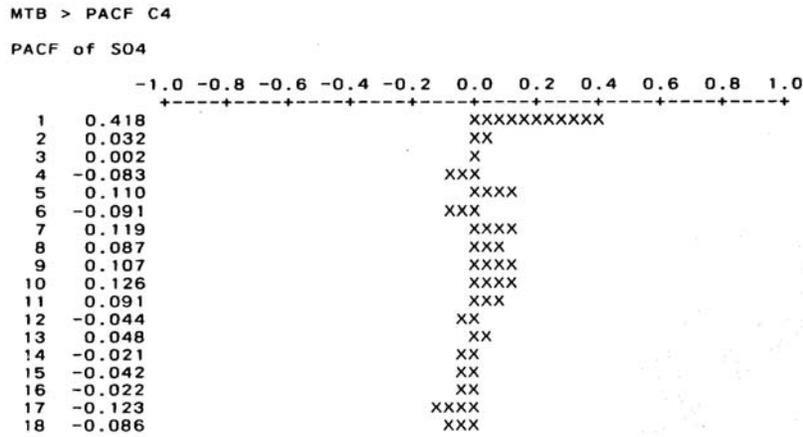


Figure 7.5i: Autocorrelation Function of Iron

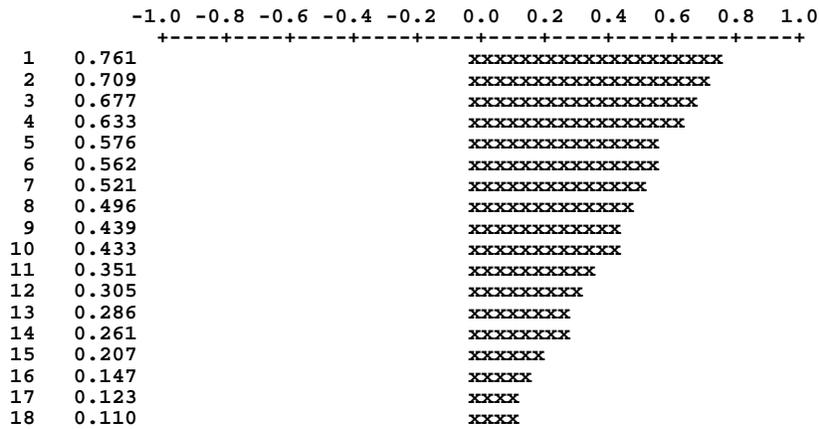


Figure 7.5j: Partial Autocorrelation Function of Iron

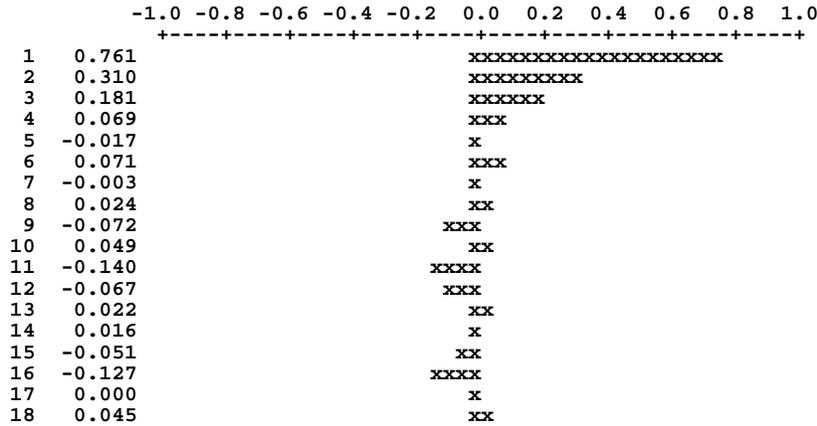


Figure 7.5k: Autocorrelation Function of Manganese

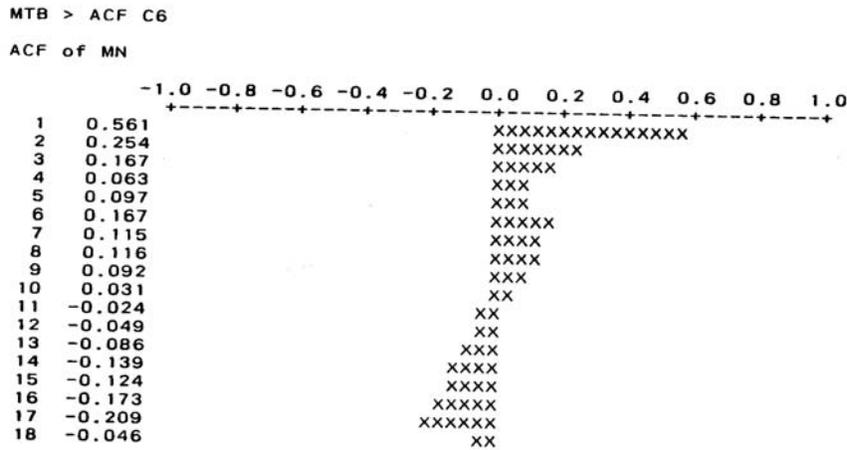


Figure 7.5l: Partial Autocorrelation Function of Manganese

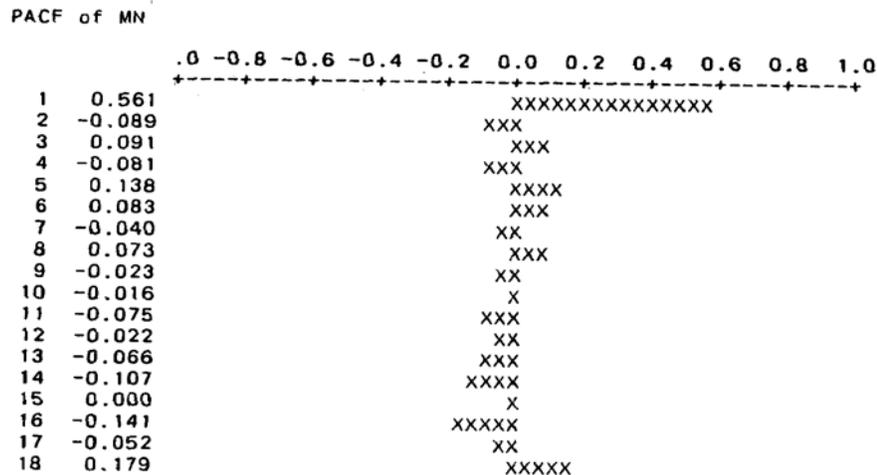


Figure 7.5m: Autocorrelation Function of Aluminum

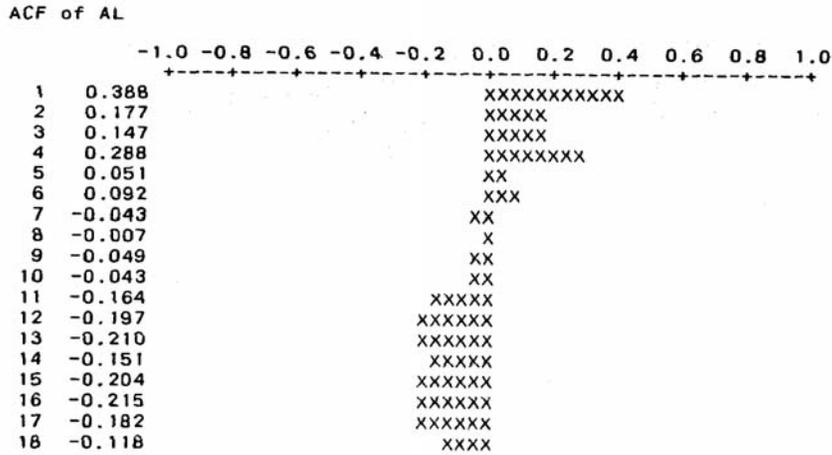
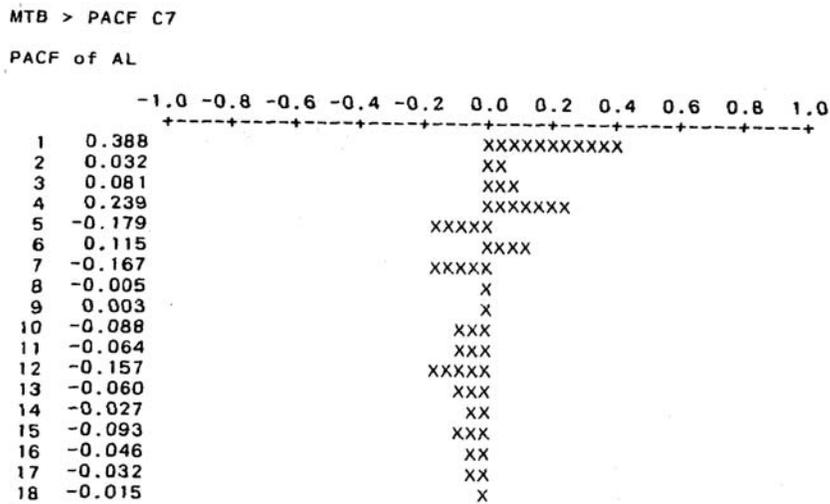


Figure 7.5n: Partial Autocorrelation Function of Aluminum



Box-Jenkins Modeling of Variation in the Seven Variables

On the basis of the above diagnostics, variation in flow was modeled using both the AR (1,0,0) and MA (0,0,1) models. Tests of the AR (1) model outcome showed no correlation between the mean and the AR coefficient ($\hat{\Phi}_1$). The residual possessed a chi-square of 9.16 with 22 degrees of freedom (df), yielding a probability of greater than 0.99 that the residual variation is white noise. Both the Acf and Pacf of the residuals were free of unusual spikes. The relationship is shown in Table 7.5. The residual standard deviation is $\hat{\sigma}_e = 0.356$ compared with an original standard deviation of $\hat{\sigma} = 0.373$, a small improvement.

Table 7.5: Equations of Models Fitted to Variables from the Fisher Deep Mine

			$\hat{\sigma}_e$	$\hat{\sigma}$
1a.	Flow AR (1)	$z_t = 0.336z_{t-1} + 1.791 + a_t$	0.356	0.373
1b.	Flow MA (1)	$z_t = 1.788 + a_t + 0.340a_{t-1}$	0.354	
2.	Acid MA (1)	$z_t = a_t - 0.533a_{t-1}$	0.119	0.218
3.	SO ₄ MA (1)	$z_t = 2.532 + 0.375a_{t-1} + a_t$	0.197	0.212
4a.	Fe AR (1)	$z_t = 0.850z_{t-1} + 0.044 + a_t$	0.252	0.411
4b.	Fe MA (1)	$z_t = z_{t-1} + a_t - 0.612a_{t-1}$	0.219	
5.	Mn MA (1)	$z_t = z_{t-1} + a_t - 0.551a_{t-1}$	0.151	0.172
6.	Al MA (1)	$z_t = 0.495 + a_t + 0.325a_{t-1}$	0.333	0.354

In the MA(0, 0, 1) model, there is no correlation between the mean and the moving average coefficient. The chi-square of the residuals is 8.879 with 22 df, a probability of $P > 0.99$ against white noise. (The resulting equation is given in Table 7.5, 1b). The residual standard deviation is 0.354, which is very close to the AR value of 0.356. The models have similar equations and similar residual errors.

Variation in acidity requires a first difference. When an MA (0,1,1) model is fitted, the chi-square of the residuals equals 22.43 with 23 df. The probability that this would arise from a white noise series is $0.50 > P > 0.30$. The equation is presented in Table 7.5, number 2, and yields a residual standard deviation of 0.119 compared with an original standard deviation of 0.218, an almost 50% improvement.

The MA (0,0,1) model was fitted to the variation in sulfate concentration. The mean is linearly independent of the MA coefficient. Chi-square = 14.87 with 22 df, clearly showing ($0.90 > P > 0.80$) that the residual variation is not different from that of white noise. The equation is shown

as No. 3 in Table 7.5 and the residual standard deviation is $\hat{\sigma}_e = 0.197$ compared with an original standard deviation of 0.212, showing little improvement.

Two models were fitted to evaluate variation in iron concentration, an AR (1,0,0) and an MA (0,1,1). An AR(1) coefficient may be a fair approximation of the first difference in the MA model. The mean is relatively small, thus the AR(1) model is not as suitable as the MA (0,1,1) fitted to first differences mean set equal to zero. The standard deviations are 0.245 for the AR model and 0.219 for the MA model compared with $\hat{\sigma} = 0.411$ for the original variable, an improvement of nearly 50 percent.

Since manganese varies in a manner similar to iron, the MA model was fitted to the first differences MA (0,1,1). The chi-square equals 23.82 with 23 df (or $0.50 > P > 0.30$, i.e., the residual variation is likely to be white noise). One significant spike at lag 4 remained in the Acf of the residuals. The equation of the MA (0,1,1) model is in Table 7.5. The standard deviation is 0.151 compared with an original standard deviation of 0.172, an improvement of only 10 percent.

Aluminum variation did not require a first difference thus the MA (0,0,1) model was fitted. Chi-square of the residuals equals 25.71 with 22 df, $0.30 > P > 0.20$. There is no correlation between the mean and the moving average coefficient. There is a significant spike at lag 4 as in the manganese model. The equation is given as No. 6 in Table 7.5. The standard deviation equals 0.333 compared with $\hat{\sigma} = 0.354$ for the original series (a marginal improvement).

These variables appear to show two patterns of variation. The first pattern is simple MA(1) performance. The second pattern is a consistent trend, usually a decline, with time. This second pattern is best matched by the MA(1) model of the first differences. The effects of the trend are removed by taking first differences. In several cases, there is a significant spike at lag 4 in the Acf of the residuals. However, this single spike is not repeated and there is no seasonal effect. No further analysis was performed because the large gaps in the time between observations prevented any more rigorous analysis.

Quality Control

The appropriate use of quality control (particularly in the form of confidence limits around the mean or median) is illustrated in Figures 7.2c and 7.2d. This enables comparison between pre-remining and post-remining water quality conditions and allows for differences in sample size.

The two standard deviation limits around the mean are also inserted in the time series plots (Figures 7.4b to 7.4g). These are confidence limits based on a sample size of one (i.e., $\bar{X} \pm 2\hat{\sigma}$). They do not appear to be very informative; very few observations fall outside these limits. In the pre-remining period, there is a tendency for the range (and the variance, see F-tests discussed earlier in this chapter) to be very much larger than after remining commences. As a result, all the observations after remining tend to fall within these rather wide limits.

Summary

The most important outcome of this analysis is to show that the pattern of variation in these six variables falls into two groups. The first group (flow, sulfate, and aluminum) appears to be unaffected by remining. The second group (acidity, iron, and manganese) shows a marked improvement after remining begins. This improvement is shown in both means (medians) and variances. The means are lower and the variances less after remining began than prior to remining.

Chapter 8: Analysis of Data from the Markson Deep Mine Site, Schuylkill County, PA

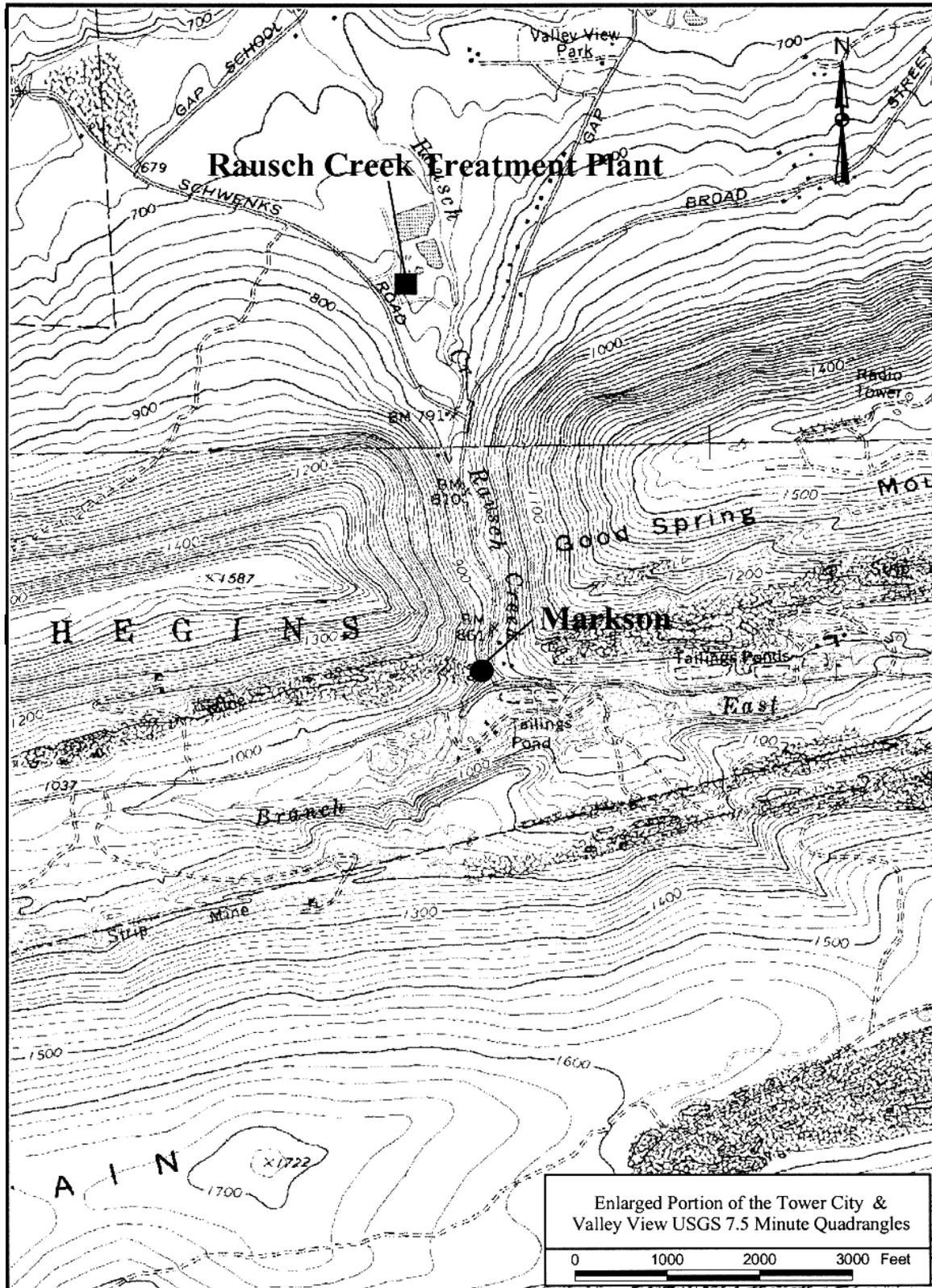
The abandoned Markson Colliery workings are located within the Donaldson Syncline of the Southern Anthracite Coal Field. The Markson discharge is located approximately 1.2 miles upstream from the Rausch Creek Treatment Plant operated by PA DEP in Schuylkill County (Figure 8.0). This discharge emanates from an airway of the abandoned Markson Colliery, and is a principal contributor to the total acid load treated at the plant. The flow and water quality characteristics of the Markson discharge were previously described in Smith (1988), Hornberger et al. (1990), and Brady et al. (1998). The data set used in most of those studies and in this chapter was collected by the Pennsylvania Department of Environmental Protection, Bureau of Abandoned Mine Reclamation (BAMR) which operates the Rausch Creek Treatment Plant. BAMR routinely samples and monitors the Markson discharge and another large abandoned deep mine discharge (Valley View Tunnel discharge) for purposes related to treatment plant operations. Additional data and discussion of the flow and water quality characteristics of the Markson discharge from 1992 to 1999 are contained in Section 5 of the EPA *Coal Remining Statistical Support Document*.

The Markson discharge exhibits water quality characteristics that differ greatly from those of principal discharges from adjacent mines (e.g., the Orchard Airway discharge from the Good Spring No. 1 Colliery and the Tracy Airway discharge from the Good Spring No. 3 Colliery). The pH of the Markson discharge ranges from 3.2 to 3.7, while the pH of the Tracy discharge ranges from 5.7 to 6.5. The distinct chemical differences in two discharges from similar abandoned underground mines in the same coal seams and the same geologic structure are attributable to stratification of large anthracite deep minepools. The Tracy discharge is a “top-water” discharge from a relatively shallow ground water flow system (at elevation 1153 feet), while the Markson discharge emanates from “bottom water” at a much lower elevation (865 feet) in the minepool system. Additional information on the chemical characteristics of stratified anthracite minepools is found in Barnes et al. (1964), Ladwig et al. (1984) and Brady et al. (1998).

The raw data for the Markson discharge are listed in Appendix F. There are 253 observations, and the assembled set is comprised of data on nine parameters as follows: days; flow; pH; acidity; iron; manganese; aluminum; sulfate; ferrous iron. Days were calculated as the number of days between the day an observation was collected and the day the first observation was collected.

The first step was to adjust the data set for missing observations. The first 147 dates had no observations for flow. The original data were, therefore, subdivided into two sets: the first consisting of eight variables (253 observations); and the second consisting of nine variables, including flow (107 observations). A tenth variable (interval) was added by taking the first differences among days to determine the regularity of the intervals between observations.

Figure 8.0: Map of Markson Site



Univariate Analysis

The two data sets (N = 253 and N = 107) were explored initially to determine the shape of the frequency distributions. The variables flow, acidity, aluminum, and ferrous iron were considered to be asymmetric and were transformed to base 10 logarithms. The summary statistics for these data sets following log transformation are shown in Table 8.1 (N = 107) and Table 8.2 (N = 253).

Table 8.1: Summary Statistics (N=107)

	N	N*	Mean	Median	Trimmed Mean	Standard Deviation	Standard Error of the Mean
Intervals	106	1	7.0660	7.0000	7.0208	0.7840	0.0761
Log Flow	107	0	3.1250	3.0892	3.1089	0.1950	0.0188
pH	107	0	3.2458	3.2000	3.2443	0.0954	0.0092
Log Acidity	107	0	1.9960	2.0000	1.9986	0.0743	0.0072
Total Iron	107	0	27.770	27.006	27.680	9.255	0.895
Mn	107	0	4.8971	4.9700	4.8920	0.9498	0.0918
Log Al	107	0	0.2961	0.3191	0.2988	0.1625	0.0157
SO ₄	107	0	272.81	271.00	272.41	27.13	2.62
Log Ferrous Iron	105	2	1.3275	1.3979	1.3489	0.2583	0.0250

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Intervals	5.0000	14.0000	7.0000	7.0000	---
Log Flow	2.8791	3.8151	2.9930	3.1978	6.2
pH	3.1000	3.5000	3.2000	3.3000	2.9
Log Acidity	1.5051	2.1818	1.9638	2.0414	3.7
Total Iron	6.900	49.871	21.500	33.762	33.3
Mn	1.2000	8.1600	4.4240	5.3100	19.4
Log Al	-0.1244	0.7686	0.1793	0.3979	54.9
SO ₄	210.00	348.00	253.00	292.00	9.9
Log Ferrous Iron	0.5185	1.6758	1.2087	1.5197	75.3

N* = Number of missing data points in data set

Table 8.2: Summary Statistics (N = 253)

	N	N*	Mean	Median	Triggered Mean	Standard Deviation	Standard Error of the Mean
Intervals	252	1	7.333	7.000	7.044	1.910	0.120
Log Flow	107	146	3.1250	3.0892	3.1089	0.1950	0.0188
pH	253	0	3.2362	3.2000	3.2209	0.1508	0.0095
Log Acidity	252	1	2.0515	2.0414	2.0483	0.1123	0.0071
Total Iron	253	0	30.703	28.997	30.410	13.026	0.819
Mn	249	4	5.0439	5.1000	5.0470	0.8351	0.0529
Log Al	246	7	0.34588	0.35622	0.35099	0.14314	0.00913
SO ₄	253	0	297.87	293.00	296.84	44.85	2.82
Log Ferrous Iron	241	12	1.3656	1.4393	1.3865	0.3056	0.0197

	Minimum	Maximum	First Quartile	Third Quartile	Coefficient of Variation
Intervals	5.000	28.000	7.000	7.000	---
Log Flow	2.8791	3.8151	2.9930	3.1978	6.2
pH	3.0000	4.4000	3.1000	3.3000	4.7
Log Acidity	1.4771	2.5340	2.0000	2.0197	5.5
Total Iron	3.810	63.500	21.045	39.656	42.4
Mn	1.2000	8.1600	4.6300	5.4200	19.8
Log Al	-0.12436	0.76864	0.28358	0.43497	41.4
SO ₄	155.00	510.00	265.00	325.50	15.1
Log Ferrous Iron	-0.1805	1.8037	1.2015	1.5798	22.4

N* = Number of missing data points in data set

The next step was examination of the regularity in the intervals between observations, (i.e., in Table 8.2; the mean is 7.33 days and the median is 7.0 days). The majority of the observations were taken at seven-day intervals as expected. The range was from 5 to 28 days, however, and from the histogram (Figure 8.1a) there were seven intervals of eight days, five intervals of six days, and one interval of five days. The regularity of these observations is desirable yet surprising. It is recommended that determination of the first differences of days should become a routine procedure for long series of observations in order to examine the regularity of sampling intervals.

The next step concerns the magnitude of variation as measured by the coefficient of variation in percent. It should be noted (see Tables 8.1 and 8.2) that when the CV% is calculated [$CV\% = (\sigma / \text{mean}) * 100$] after logs have been taken, the mean values tend to be rather low. This will automatically inflate the CV%. It is suspected that this is the case with aluminum and ferrous

iron in both data sets. Most of the variation is very low for flow, pH, and acidity (less than 10%). Only iron, ferrous iron, and aluminum have high CV% values. This is largely due to low mean values rather than high standard deviations.

The frequency distributions of selected variables from these data sets are shown in Figures 8.1a through 8.1i. The number of samples represented in the histograms for each parameter ranges from N = 106 (interval) to N = 253 (sulfate) depending on the number of sample results reported for the corresponding parameter. The histogram for log flow, with N = 107 (Figure 8.1b), is skewed right even after taking logs. The histogram of each data set (N = 252 and N = 107) for log acidity appears fairly regular with some negative skewness after taking logs (Figures 8.1c and 8.1d). The data sets of both iron and manganese result in symmetrical histograms (Figures 8.1e and 8.1f, respectively). Aluminum is symmetrical after taking logarithms (Figure 8.1g) whereas, sulfate is essentially symmetrical without transformation (Figure 8.1h). Ferrous iron is strongly negatively skewed after taking logarithms (Figure 8.1i), making further analysis of this variable suspect.

Figure 8.1a: Histogram of Interval (N=106)

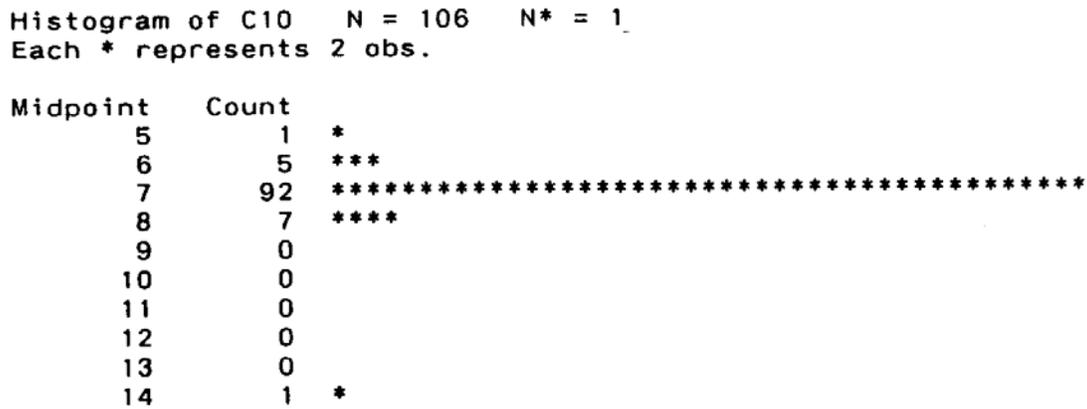


Figure 8.1b: Histogram of Log Flow (N=107)

```

Histogram of FLOW   N = 107

Midpoint   Count
  2.9       22 *****
  3.0       18 *****
  3.1       33 *****
  3.2       15 *****
  3.3        5 *****
  3.4        5 *****
  3.5        4 ****
  3.6        2 **
  3.7        2 **
  3.8        1 *

```

Figure 8.1c: Histogram of Log Acidity (data set N=252)

```

Histogram of ACID   N = 252   N* = 1
Each * represents 5 obs.

Midpoint   Count
  1.5        2 *
  1.6        0
  1.7        1 *
  1.8        1 *
  1.9       18 ****
  2.0      112 *****
  2.1       87 *****
  2.2       19 ****
  2.3        8 **
  2.4        2 *
  2.5        2 *

```

Figure 8.1d: Histogram of Log Acidity (data set N=107)

```

Histogram of ACID   N = 107

Midpoint   Count
  1.50      1 *
  1.55      0
  1.60      0
  1.65      0
  1.70      0
  1.75      0
  1.80      0
  1.85      0
  1.90      9 *****
  1.95     30 *****
  2.00     31 *****
  2.05     26 *****
  2.10      8 *****
  2.15      1 *
  2.20      1 *

```

Figure 8.1e: Histogram of Iron (N=253)

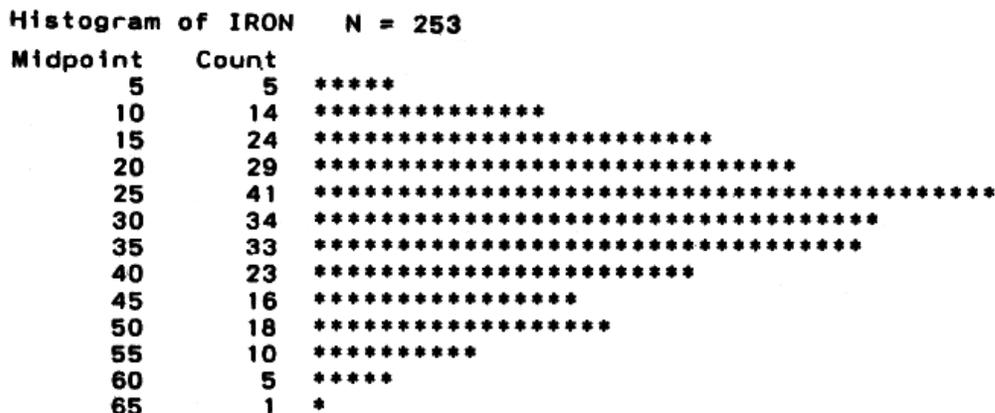


Figure 8.1f: Histogram of Manganese (N=249)

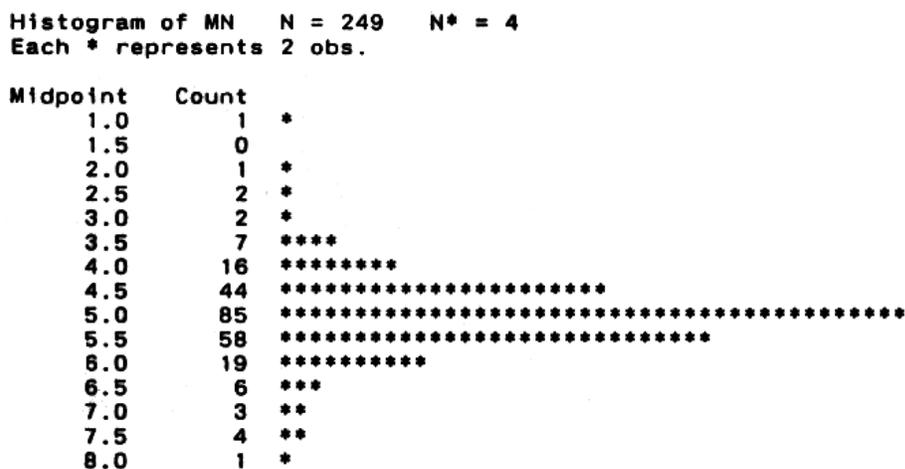


Figure 8.1g: Histogram of Log Aluminum (N=246)

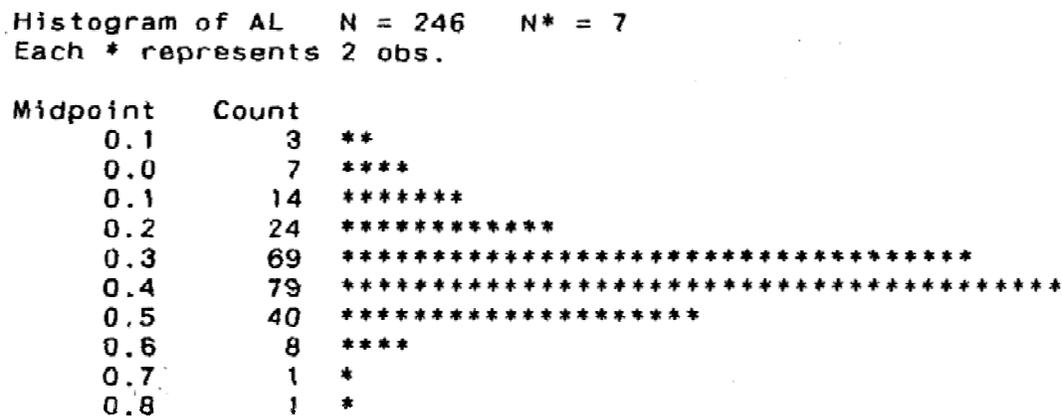


Figure 8.1h: Histogram of Sulfate (N=253)

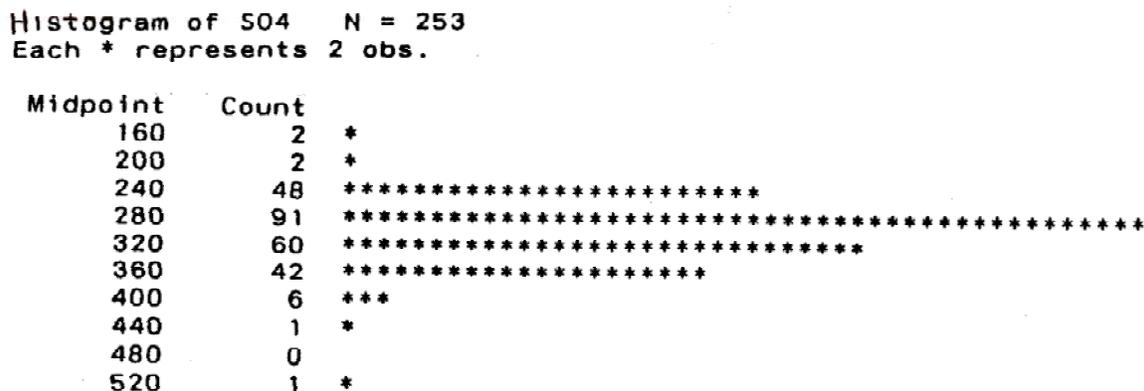
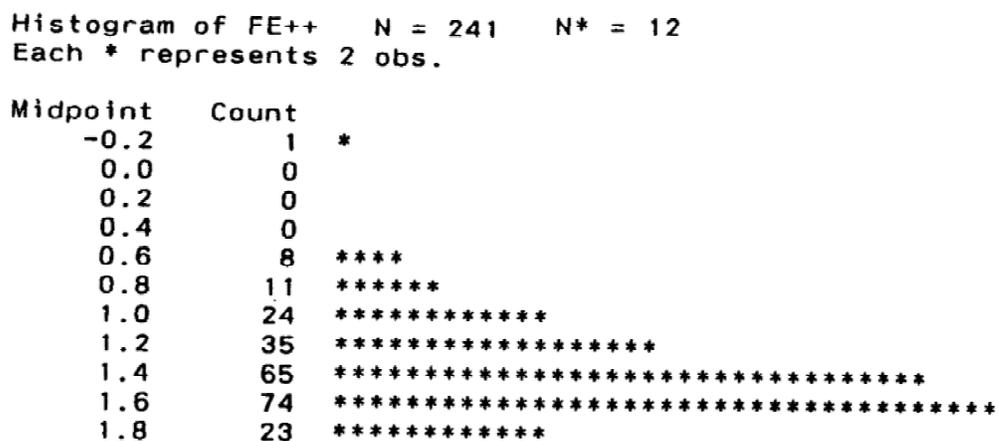


Figure 8.1i: Histogram of Log Ferrous Iron (N=241)



Bivariate Analysis

The interrelationships among pairs of variables are summarized in Tables 8.3 (N = 107) and 8.4 (N = 253). The critical level of the correlation coefficient for N = 107 is 0.195. Any r less than 0.195 is not significantly different from zero. For the data set with N = 253, any pair with r less than 0.15 is not significantly different from zero. These critical values are inserted above each table. It was found that the degree of association is best measured by the correlation coefficient squared = r^2 %. Due to the large size of the data set, a correlation as low as $r = 0.2$ can be considered statistically significant. However, a correlation of $r = 0.2$ yields $r^2 = 0.04$ (i.e., only 4% of the variation of one parameter can be explained by the other parameter). Therefore, a higher $r = 0.4$ ($r^2 = 16\%$) was arbitrarily chosen to determine the lower limit of interest.

Table 8.3: Correlations Among Variables (N = 107)

r < 0.195 not significantly different from 0									
	Days	Log Flow	pH	Log Acidity	Iron	Mn	Log Al	SO ₄	Log Ferrous Iron
Log Flow	0.422								
pH	0.536	0.263							
Log Acidity	-0.396	-0.259	-0.191						
Iron	-0.174	-0.610	-0.075	0.211					
Mn	0.385	0.048	0.169	0.089	0.183				
Log Al	0.195	0.474	-0.027	-0.036	-0.402	0.584			
SO ₄	-0.003	-0.165	-0.087	0.264	0.359	0.322	0.095		
Log Ferrous Iron	-0.338	-0.690	-0.175	0.380	0.770	0.036	-0.424	0.400	
Interval	-0.141	-0.001	-0.119	0.016	-0.067	-0.064	0.042	0.010	0.008

Table 8.4: Correlations Among Variables (N = 253)

r < 0.15 not significantly different from 0									
	Days	Log Flow	pH	Log Acidity	Iron	Mn	Al	SO ₄	Log Ferrous Iron
Log Flow	0.422								
pH	-0.002	0.263							
Log Acidity	-0.348	-0.259	0.016						
Iron	-0.401	-0.610	0.180	0.124					
Mn	-0.036	0.048	-0.030	0.174	0.177				
Log Al	-0.227	0.474	-0.069	0.133	-0.199	0.435			
SO ₄	-0.589	-0.165	0.171	0.322	0.455	0.289	0.116		
Log Ferrous Iron	-0.334	-0.690	0.079	0.140	0.803	0.042	-0.268	0.356	
Interval	-0.100	-0.002	-0.088	0.103	-0.020	-0.058	0.027	0.030	0.018

While it is advantageous to use r^2 rather than r as an indication of the strength of any association between two variables, it is also advisable to examine scatter diagrams to see the relationship graphically displayed. Because r and r^2 are really measures of linear association, in those cases where r is low (and r^2 therefore very low), the graph may show a close curvilinear association. For example, in Figure 8.2a (sulfate vs. flow), there could be a curvilinear inverse relationship between the variables although the scatter at high flows (> 3.4) tends to mask it. Both total iron and ferrous iron are also negatively associated with flow ($r^2 = 37\%$ in both data sets, see Figure 8.2b, for example for total iron).

Manganese and aluminum show positive association in both data sets ($r^2 = 34\%$ and 16% for the 107 and 253 sample data sets respectively, Figure 8.2c). Apart from flow and manganese, there does not appear to be any meaningful relationship between aluminum and any other variable (Figure 8.2d).

Manganese and flow do not show a significant positive (i.e., $r = 0.048$) or inverse relationship (Figure 8.2e). Similarly, acidity appears to have no association with any of the other parameters (e.g., Figures 8.2f and 8.2g).

Figure 8.2a: Plot of Sulfate vs. Log Flow

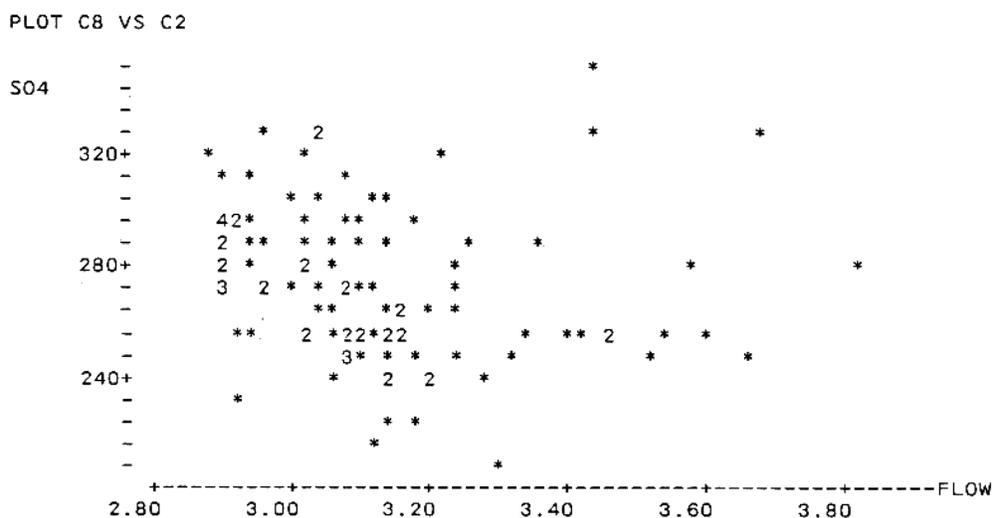


Figure 8.2b: Plot of Iron vs. Log Flow

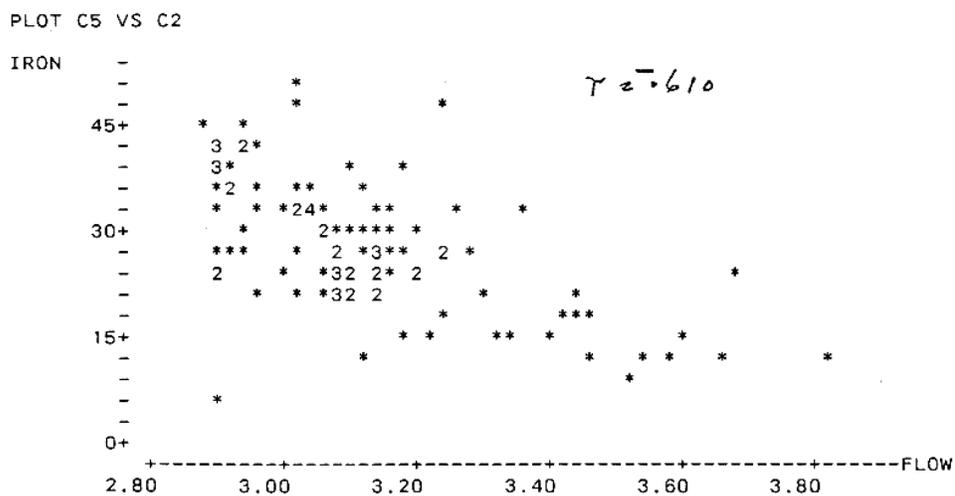


Figure 8.2c: Plot of Manganese vs. Log Aluminum

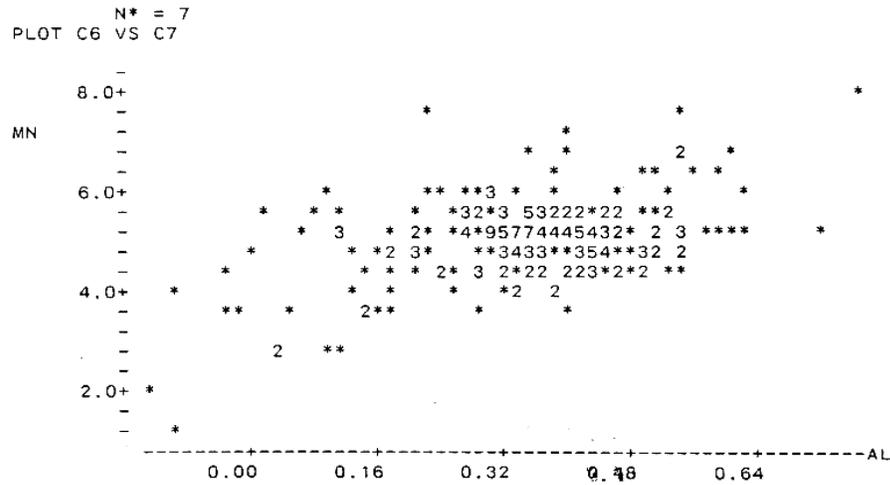


Figure 8.2d: Plot of Log Aluminum vs. Sulfate

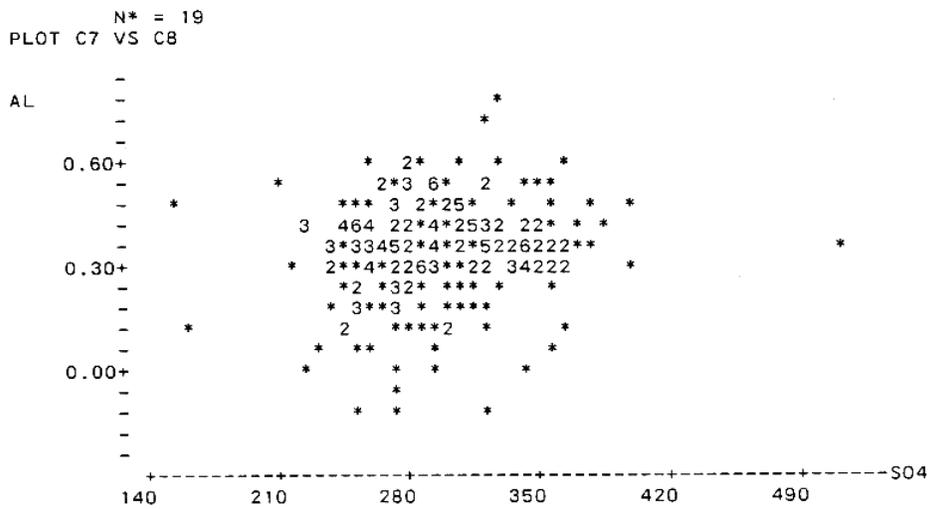


Figure 8.2e: Plot of Manganese vs. Log Flow

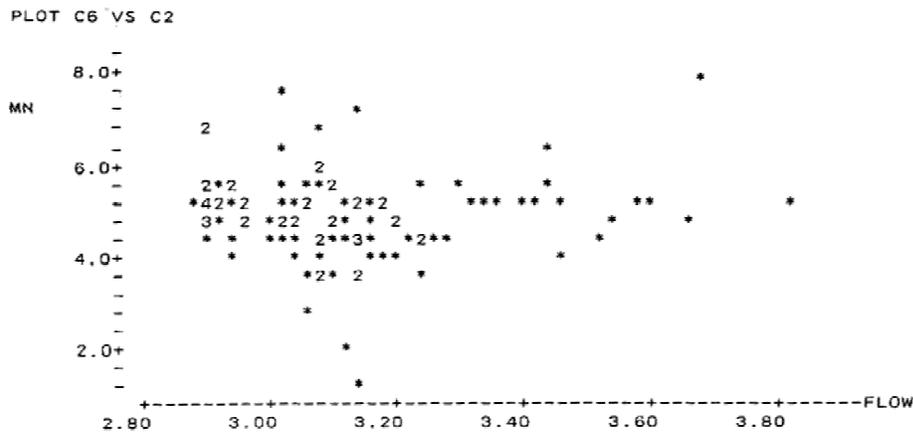


Figure 8.2f: Plot of Log Acidity vs. Log Flow

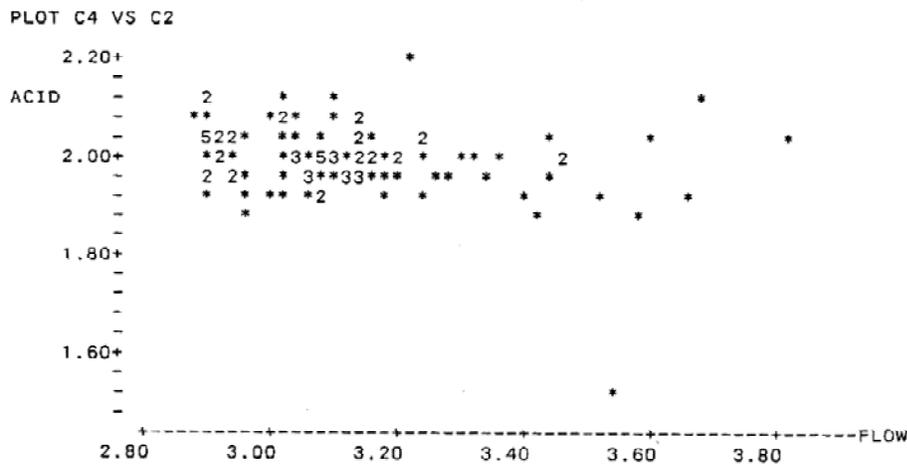
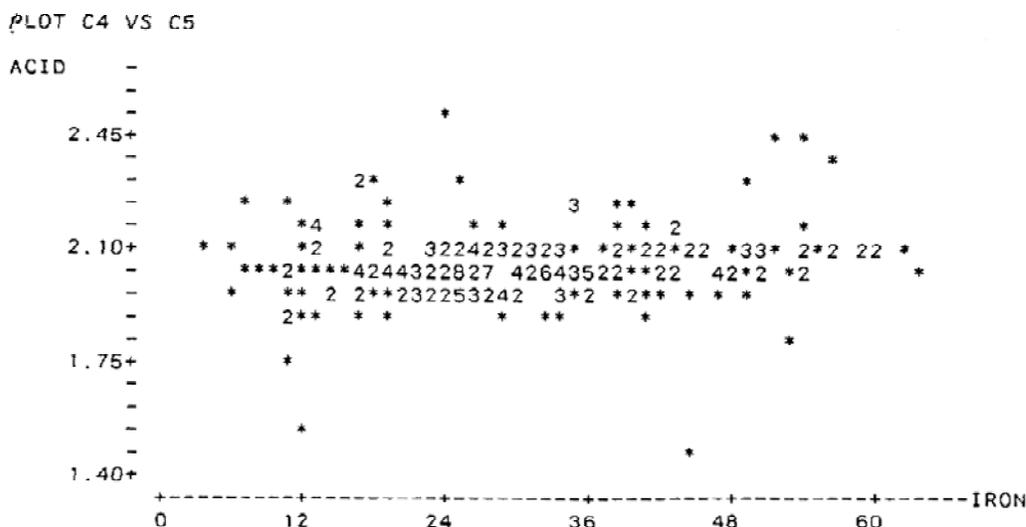


Figure 8.2g: Plot of Log Acidity vs. Iron



Since there does not appear to be any very strong relationship among these variables, they were examined in pairs using cross-correlation functions (CCF). The outcomes are summarized in Table 8.5. There do not appear to be any discrepancies between the correlation coefficient and the cross-correlation coefficient results [i.e., the relationships at zero lag (Tables 8.3 and 8.4) and at any other lags (Table 8.5)]. There are wide regions of the CCF that are above the 0.2 limits demonstrating that, for the most part, interrelationships among these variables are weak to almost non-existent. The only two that stand out are the relationships between flow and iron and iron and ferrous iron (and therefore, between flow and ferrous iron).

Table 8.5: Cross-correlations Among Variables

No.	Variables	r	lag @ r max	$ r > 0.2$
1.	pH vs. Flow	0.305	-6	- 8 to 7
2.	Acid vs. Flow	- 0.382	-5	- 13 to 0
3.	Iron vs. Flow	- 0.676	-2	- 16 to + 6, 15 to 20
4.	Mn vs. Flow	- 0.334	12	-21, -11, 7 to 20
5.	Al vs. Flow	0.475	0	- 13 to 13
6.	SO ₄ vs. Flow	- 0.502	-8	- 18 to - 1, 6 to 20
7.	Ferrous Iron vs. Flow	- 0.740	-1	- 15 to 6, 16 to 20
8.	Acid vs. pH	- 0.321	-5	- 16,- 8,- 7,- 5 to -3, -1, 2, 3
9.	Iron vs. pH	-0.175	-12	none
10.	Mn vs. pH	0.288	13	-14, 6 to 13
11.	Al vs. pH	0.232	-20	- 20
12.	SO ₄ vs. pH	0.296	11	8 to 14
13.	Ferrous Iron vs. pH	- 0.227	-13	- 14 to - 12, -10, 2
14.	Iron vs. Acid	0.226	9	0, 4, 9
15.	Mn vs. Acid	- 0.287	13	13
16.	Al vs. Acid	- 0.214	13	13
17.	SO ₄ vs. Acid	0.29	2	- 17, - 4 to 0, 2
18.	Ferrous Iron vs. Acid	0.373	0	- 2 to 6, 9, 10
19.	Mn vs. Iron	- 0.283	14	-20, 3, 14, 16 to 18, 20
20.	Al vs. Iron	- 0.562	3	- 20, -9 to 17
21.	SO ₄ vs. Iron	- 0.458	20	- 20, -18 to 2, 12 to 20
22.	Ferrous Iron vs. Iron	0.776	0	-11 to 13
23.	Al vs. Mn	0.584	0	-20 to -15, -5 to 1
24.	SO ₄ vs. Mn	0.326	-1	-2 to 1
25.	Ferrous Iron vs. Mn	- 0.281	-16	- 20 to - 15, - 10
26.	SO ₄ vs. Al	0.419	17	- 20 to - 10, -8, -7, 5, 6, 9 to 20
27.	Ferrous Iron vs. Al	- 0.478	-3	- 16 to 8
28.	Ferrous Iron vs. SO ₄	0.473	4	- 20 to - 8, -2 to 13

Time Series Analysis

One of the most striking features of the time series plots (Figures 8.3a through 8.3f) is the limited variation which they show. Another feature of interest is the unusual variation shown by log flow. The major flow event from February 1986 to July 1986 is worth noting and does not appear in any of the other graphs. This emphasizes a lack of relationship between the parameters. Clearly, there appears to be no associated variation among the parameters, except for the pair that includes iron and ferrous iron.

Figure 8.3a: Time series Plot of Flow

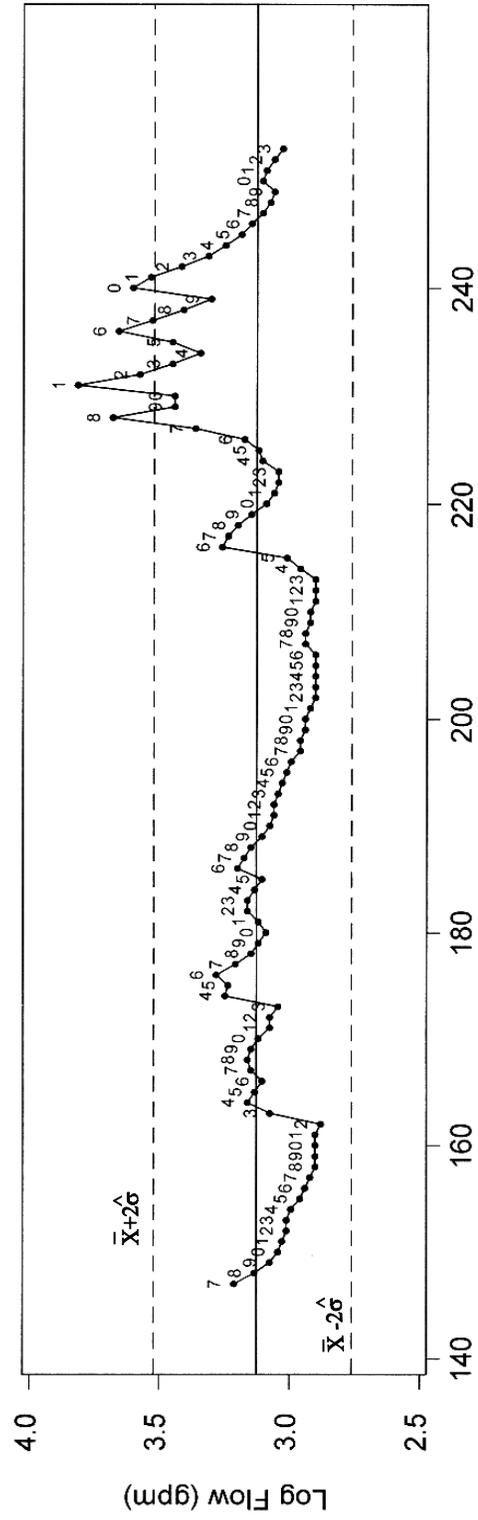


Figure 8.3b: Plot of Manganese

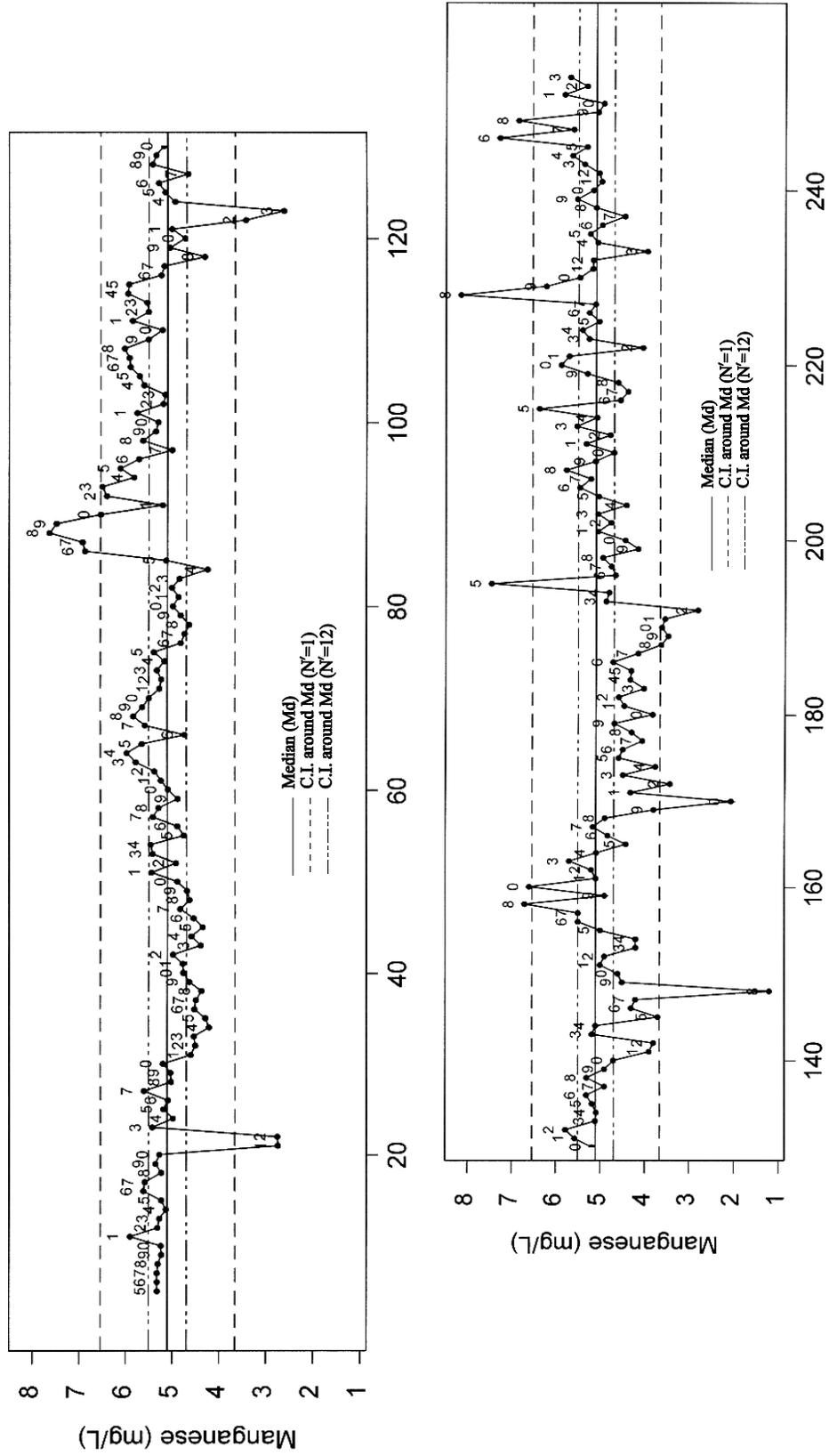


Figure 8.3c: Time Series Plot of Sulfate

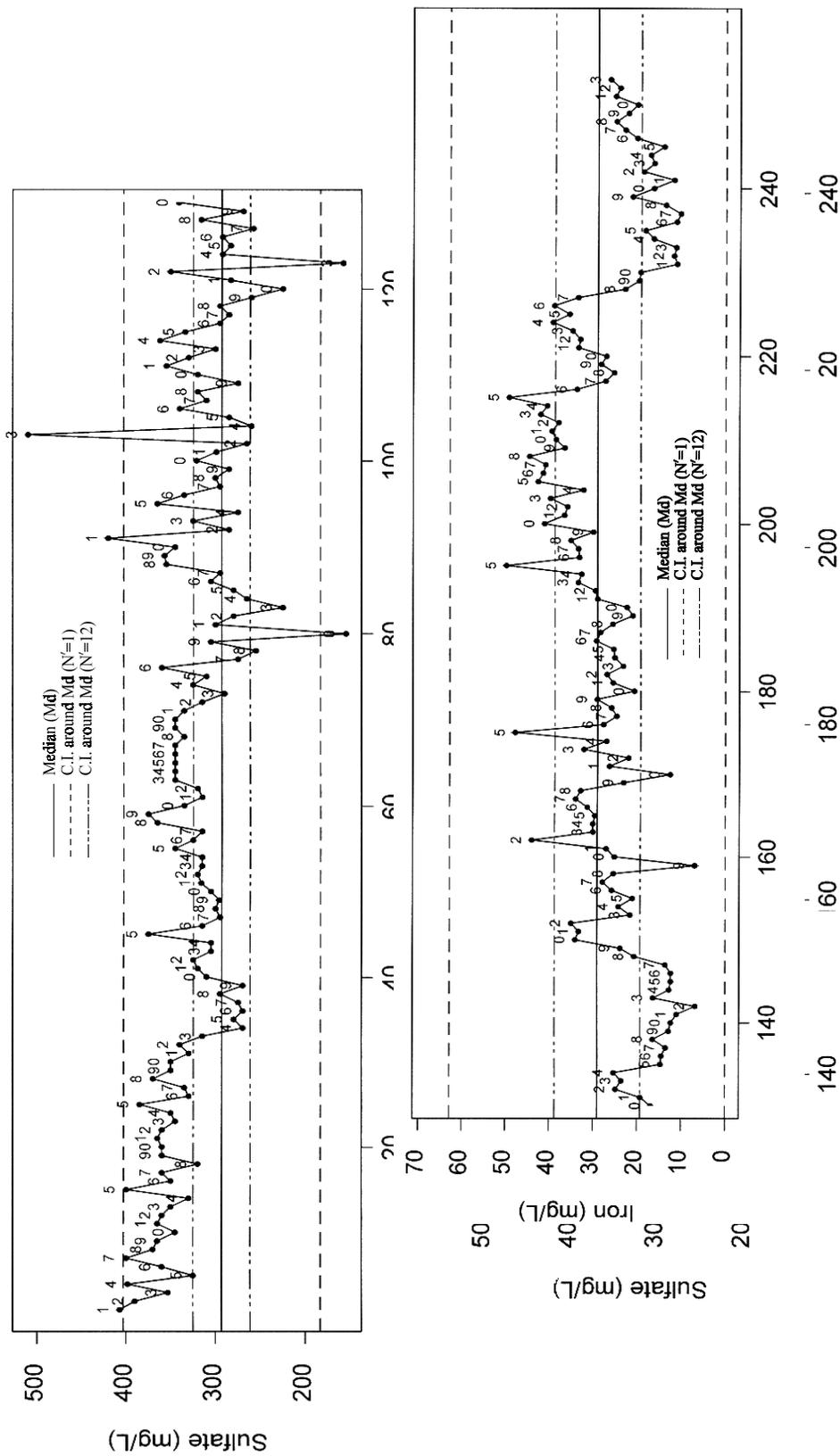


Figure 8.3d: Time Series Plot of Iron

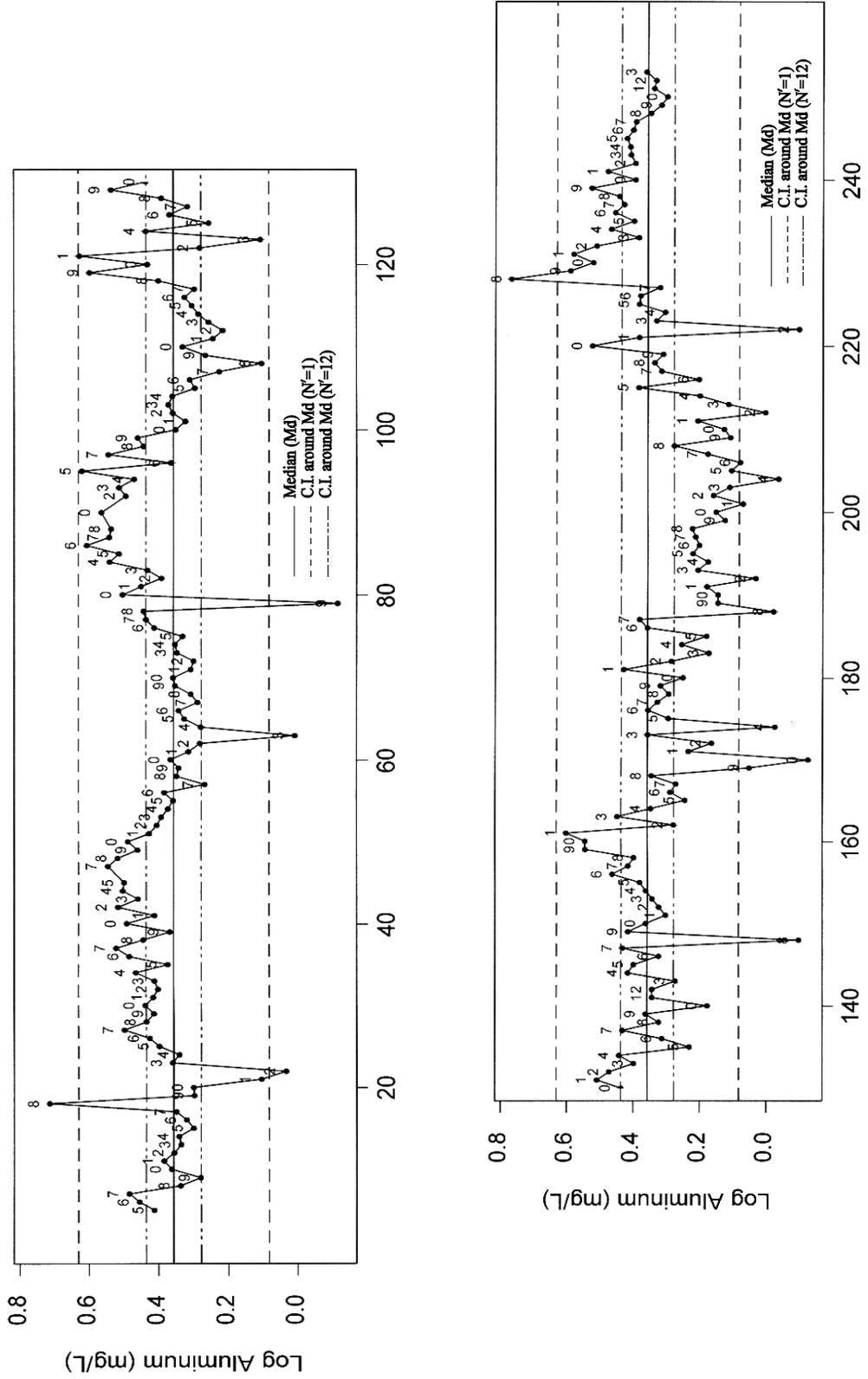


Figure 8.3e: Time Series Plot of Aluminum

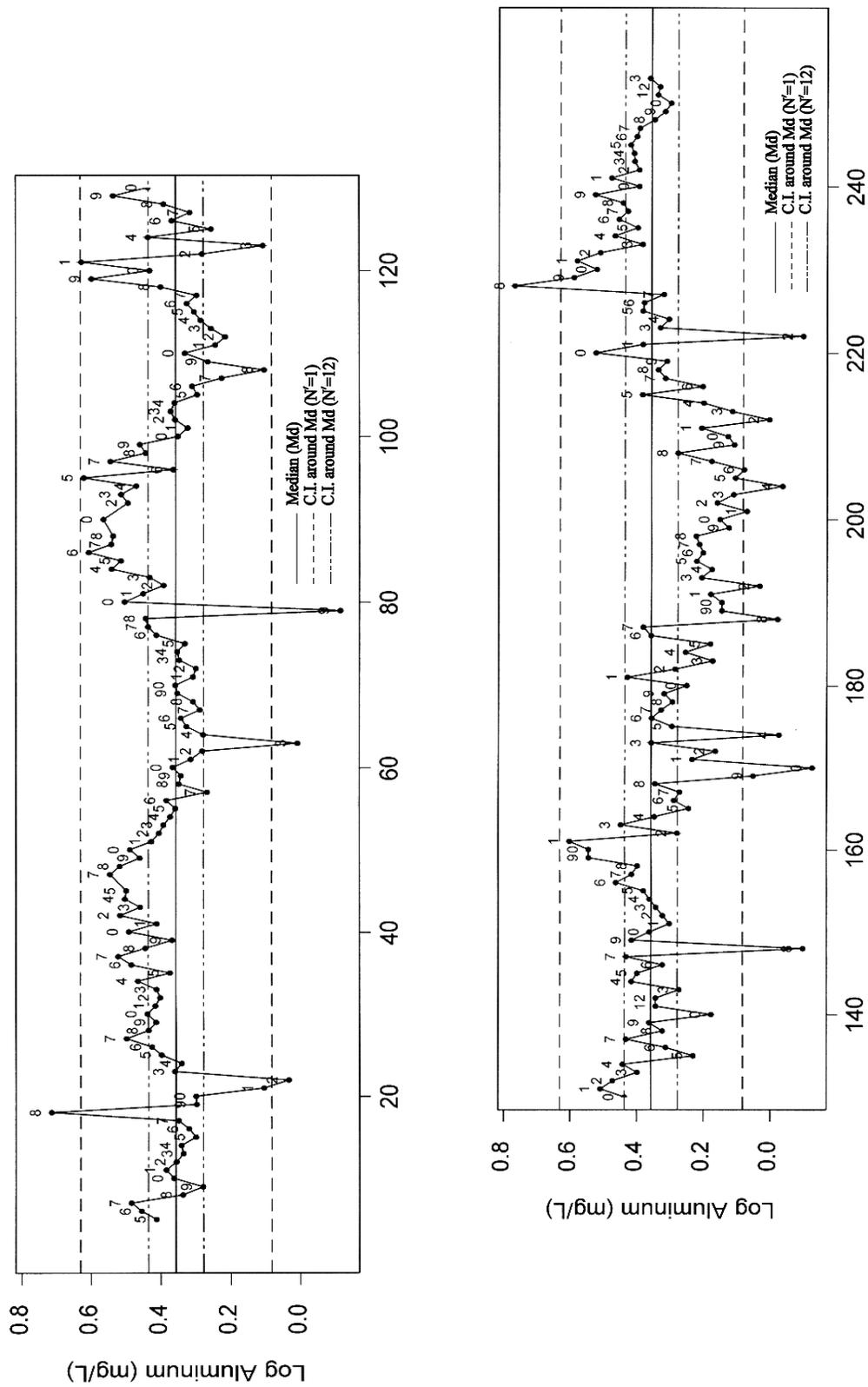
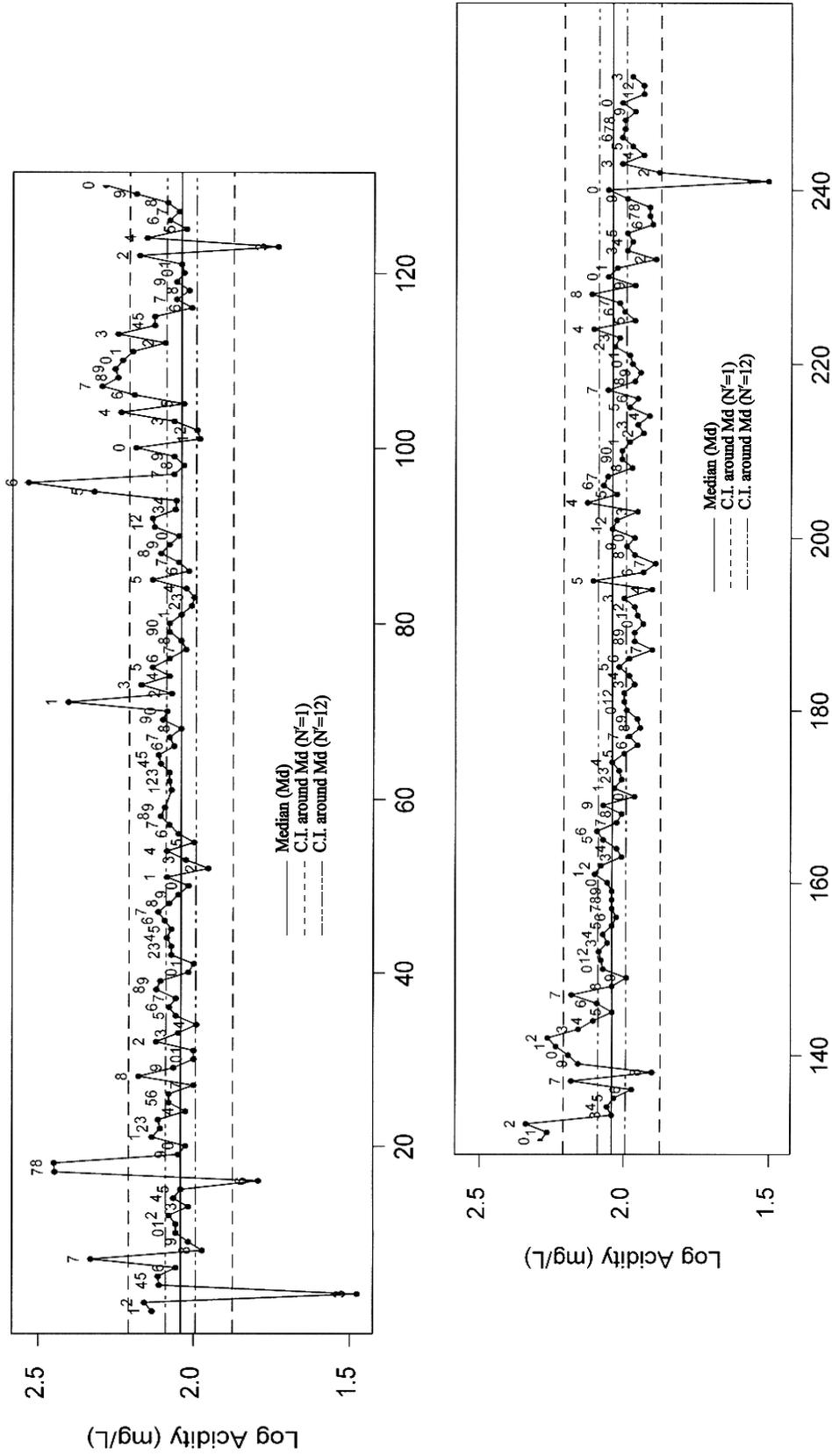


Figure 8.3f: Time Series Plot of Acidity



Quality Control Applied to the Variables

Two measures of quality control are calculated and summarized in Tables 8.6 and 8.7; in Table 8.6 the conventional two standard deviation limits around the mean are given for each of the eight variables (these limits are presented, for example, in Figure 8.3a).

Table 8.6. Quality Control Limits $\bar{X} \pm 2\hat{\sigma}$

Parameter	Mean \bar{X}	Standard Deviation $\hat{\sigma}$	$2\hat{\sigma}$	$\bar{X} \pm 2\hat{\sigma}$
Log Flow	3.125	0.195	0.39	2.76 to 3.52
pH	3.246	0.095	0.19	3.056 to 3.436
Log Acidity	1.996	0.074	0.148	1.848 to 2.144
Iron	27.770	9.285	18.51	9.20 to 46.34
Mn	4.897	0.950	1.9	2.997 to 6.797
Log Al	0.296	0.163	0.326	(-0.03) to 0.622
SO ₄	272.81	27.13	54.26	218.55 to 381.33
Log Ferrous Iron	1.328	0.258	0.516	0.812 to 1.844

**Table 8.7. Quality Control Limits: $Md \pm [1.96 * 1.25(Q_1 - Q_3)/1.35 \sqrt{N'}]$
N = 253 data set, except flow, N = 107).**

	Median	Q ₁	Q ₃	Q ₃ - Q ₁	N'	1.35* $\sqrt{N'}$	Lower Limit	Upper Limit
Log Flow	3.089	2.993	3.198	0.205	1	1.350	2.717	3.461
					12	4.677	2.982	3.196
pH	3.2	3.1	3.3	0.2	1	1.350	2.837	3.563
					12	4.677	3.095	3.305
Log Acidity	2.041	2	2.092	0.092	1	1.350	1.874	2.208
					12	4.677	1.993	2.089
Iron	28.997	21.045	39.656	18.611	1	1.350	-4.779	62.773
					12	4.677	19.247	38.747
Mn	5.1	4.63	5.42	0.79	1	1.350	3.666	6.534
					12	4.677	4.686	5.514
Log Al	0.356	0.284	0.435	0.151	1	1.350	0.082	0.630
					12	4.677	0.277	0.435
SO ₄	293	265	325.5	60.5	1	1.350	183.204	402.796
					12	4.677	261.305	324.695
Log Ferrous Iron	1.439	1.202	1.58	0.378	1	1.350	0.753	2.125
					12	4.677	1.241	1.637

Furthermore, for Table 8.7, two sample sizes are used, the first with sample size $N' = 1$ and the second with $N' = 12$. The set of quality control limits used in Figures 8.3b through 8.3f are the

limits of a confidence interval (C.I.) Around the median, based on Tukey's non-parametric formula of:

$$\text{Median} \pm [1.96 (Q_1 - Q_3) 1.25 / (1.35 \sqrt{N'})]$$

Two values of N' are used, (namely, $N' = 1$ and $N' = 12$) in Figures 8.3b, 8.3c, 8.3d, 8.3e, and 8.3f.

Many of the observations, which fall outside the limits when $N' = 1$, are single observations and need no activity to explain the exceedance. The longer areas of departure in flow (Figure 8.3a) are due to natural events and presumably, are not related to mining activity. It would be expected that this extreme and long-term departure would be reflected in the variation of the other parameters, but this is not the case.

With nearly all other parameters it appears that the control limits are somewhat tight and that most of the variation outside of the control limits is irregular and of short duration (e.g., manganese in Figure 8.3b and sulfate in Figure 8.3c).

Iron shows two relatively long term, mostly positive deviations beyond the control limits (Figure 8.3d) in the period up to observation 80 (February 20, 1986). These deviations are not repeated in later observations. Sulfate (Figure 8.3c) also extends beyond the upper limits for the first 30 observations (i.e., before February 28, 1985) and appears to decrease with time. The behavior of aluminum within the quality control limits (Figure 8.3e) is similar to manganese and sulfate. However, the aluminum values drop below the lower limit for most of the observations from 185 to 225. Acidity (Figure 8.3f) shows little variation, with a few isolated peaks extending outside the upper limits. In three cases (October 1983, March 1984 and June 1984) consecutive results exceeded the upper limit.

Model Identification

Identification of appropriate models is performed by using the autocorrelation (Acf) and partial autocorrelation (Pacf) functions of the eight parameters. There are three types of functions which can be characterized by appearance. The first type shows a strong steady decline from a high value. Flow (Figure 8.4a), iron (Figure 8.4b), aluminum (Figure 8.4d), and ferrous iron are examples of this type. All these parameters show a large spike at lag 1 in their Pacf (see iron in Figure 8.4c and aluminum in Figure 8.4e). These characteristics imply the parameter possesses a trend which must be removed before further time series analysis. Removal may be achieved by taking first differences. An example can be demonstrated using days, which increase in value throughout the period of observation. Taking first differences results in random walk characteristics (Figure 8.4f). Thus, the first difference is sufficient to make this parameter stationary.

The second type of function shows a less pronounced decline (e.g., pH (Acf in Figure 8.4g)). The Pacf of pH, however, shows a pronounced spike at lag 1, and it too requires taking first

differences to become stationary (Figure 8.4h). Manganese (Acf in Figure 8.4i) is similar to pH except its Pacf does not have a pronounced spike at lag 1 (Figure 8.4j). Therefore, an AR model may be suitable. The first coefficient ($\hat{\Phi}_1$) may suffice for the first difference.

The third type of function is represented by sulfate which appears to show a trend as well as some irregularities (Acf in Figure 8.4k). Before the irregularities can be evaluated the strong spike in the Pacf at lag 1 must be reduced (Figure 8.4l).

Figure 8.4a: Autocorrelation Function of Flow

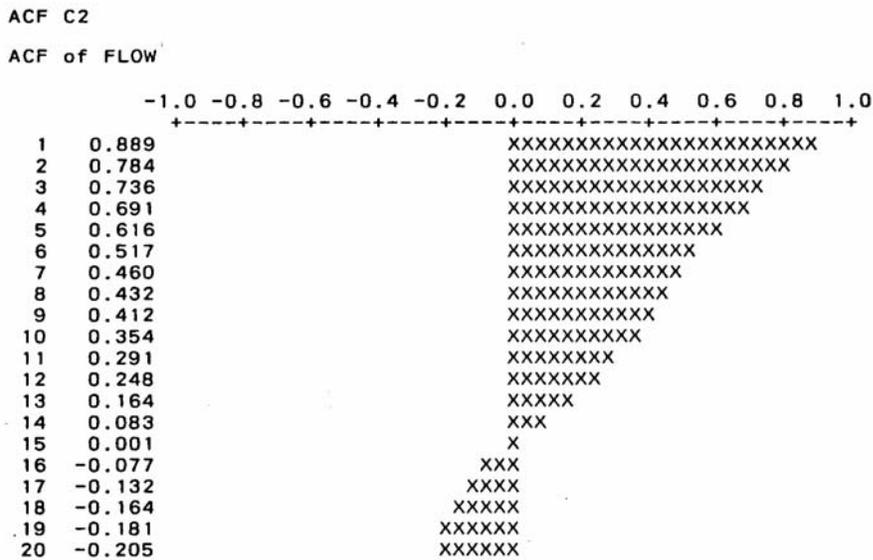


Figure 8.4b: Autocorrelation Function of Iron

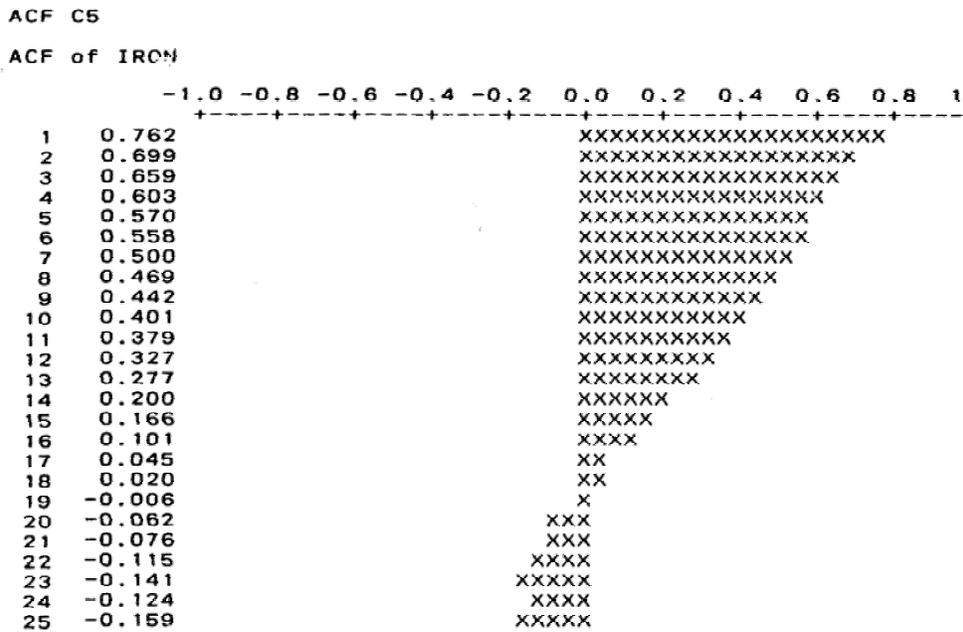


Figure 8.4c: Partial Autocorrelation Function of Iron

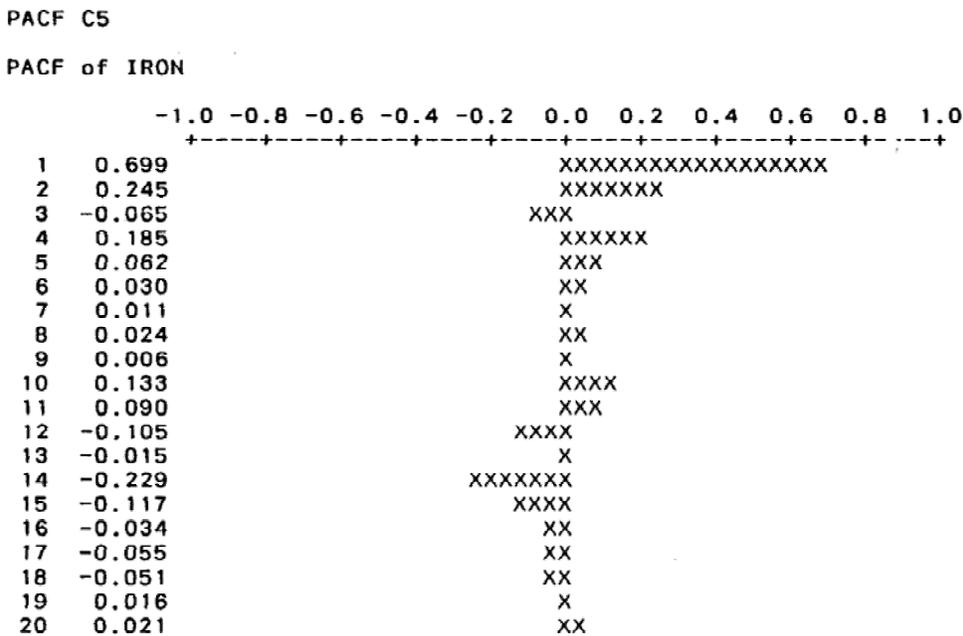


Figure 8.4d: Autocorrelation Function of Aluminum

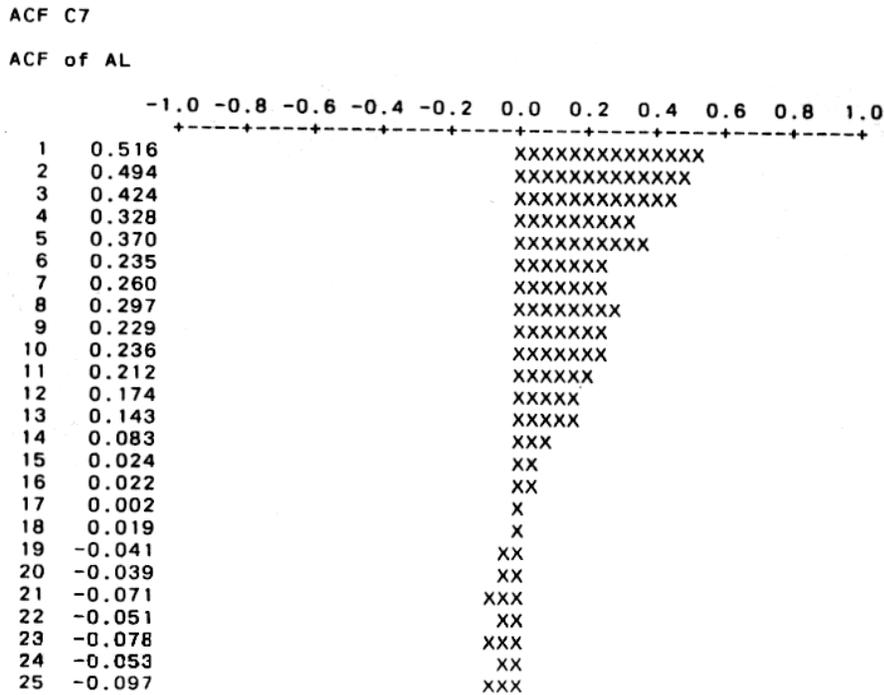


Figure 8.4e: Partial Autocorrelation Function of Aluminum

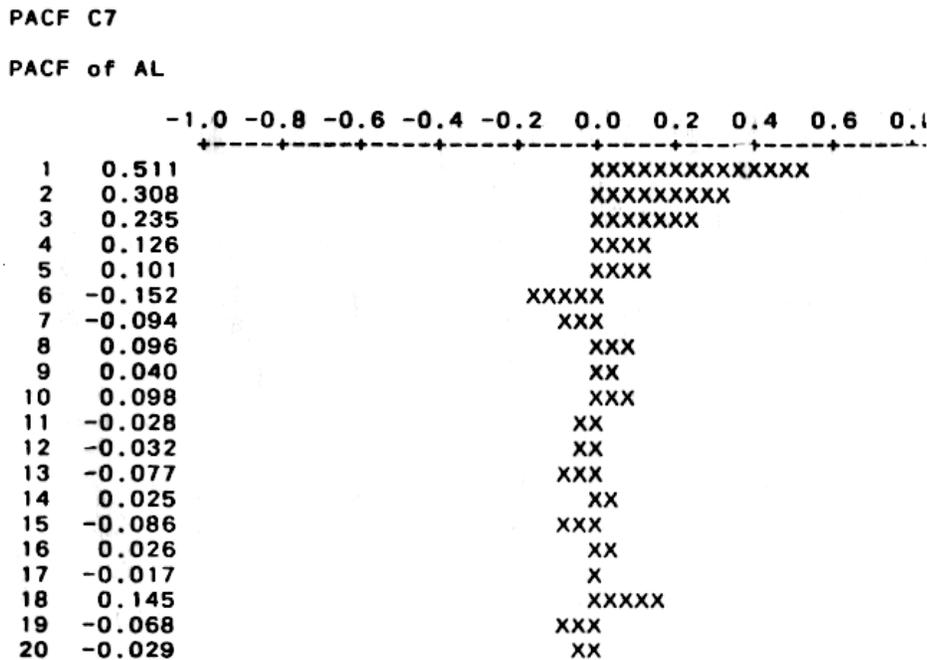


Figure 8.4f: Autocorrelation Function of Intervals

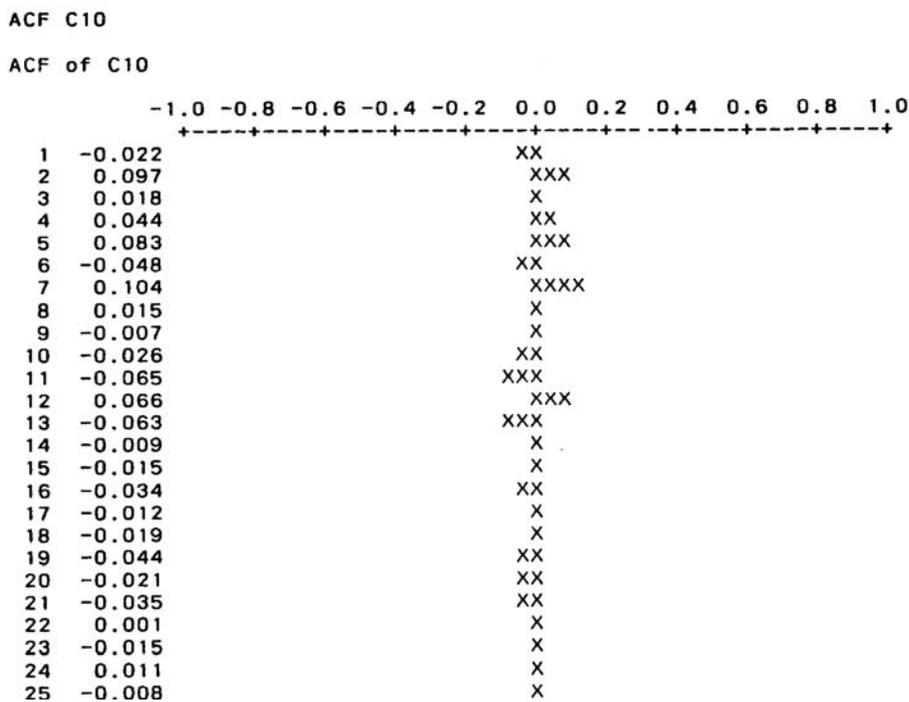


Figure 8.4g: Autocorrelation Function of pH

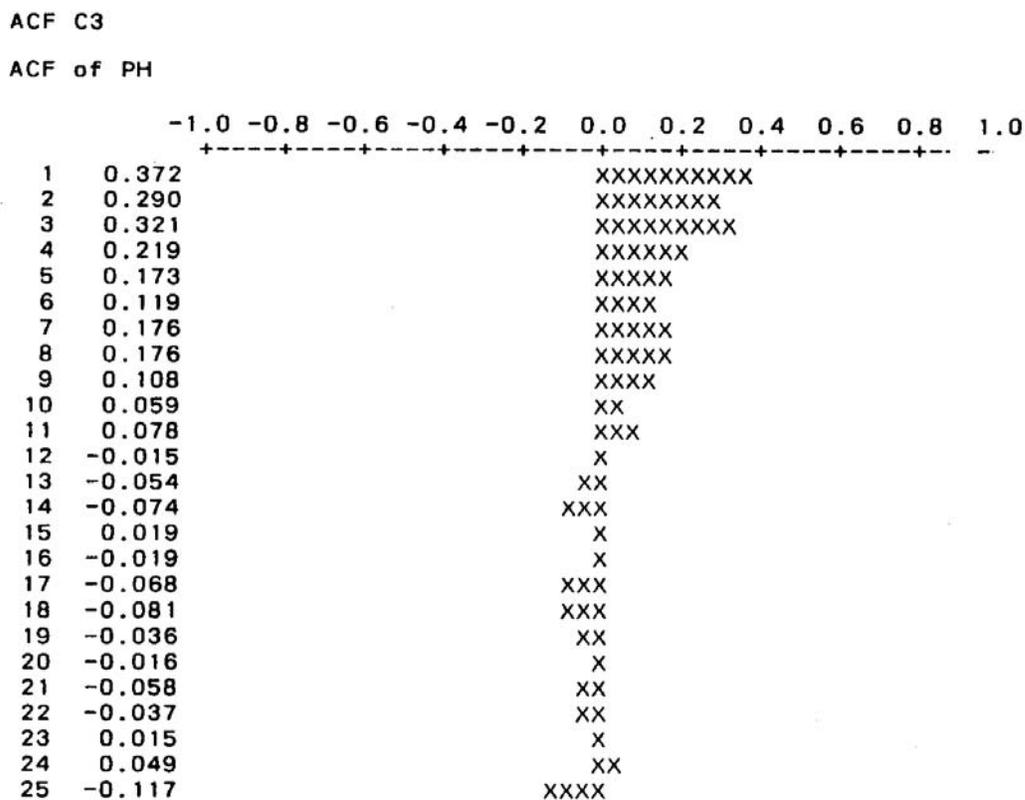


Figure 8.4h: Partial Autorcorrelation Function of pH

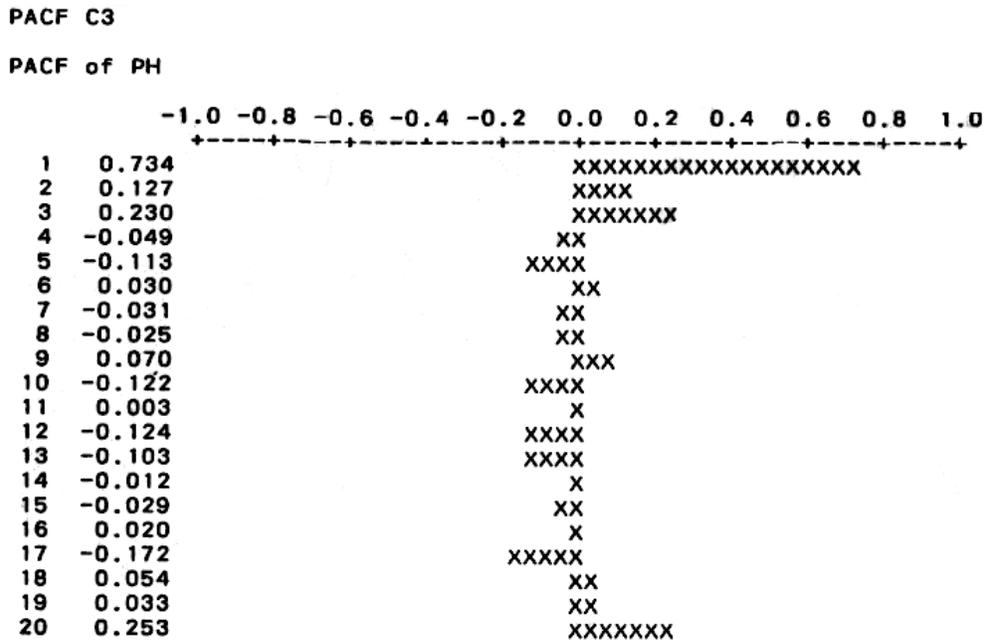


Figure 8.4i: Autocorrelation Function of Manganese

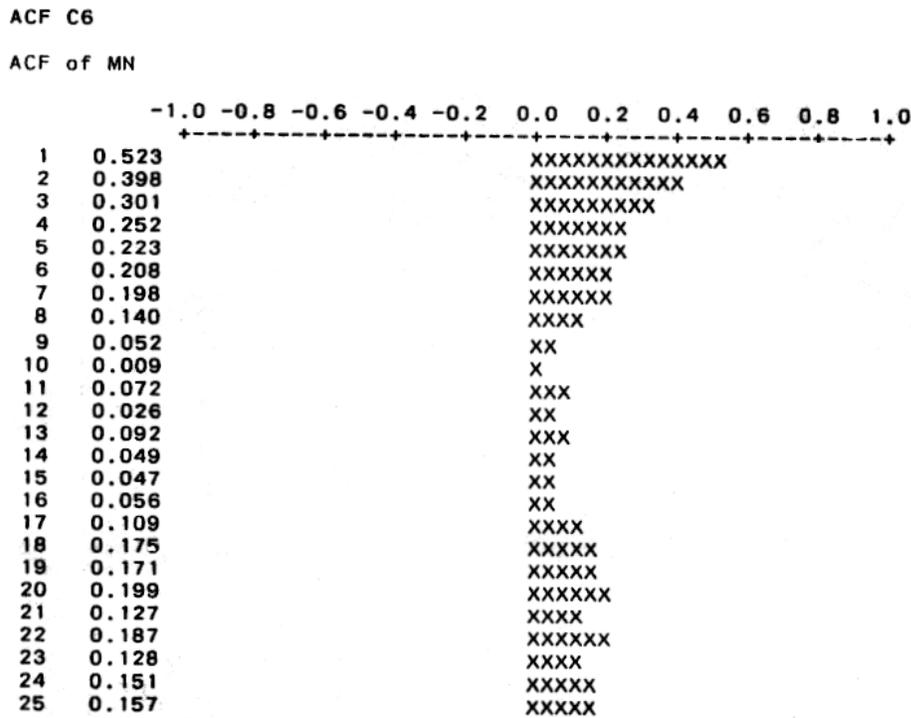


Figure 8.4j: Partial Autocorrelation Function of Manganese

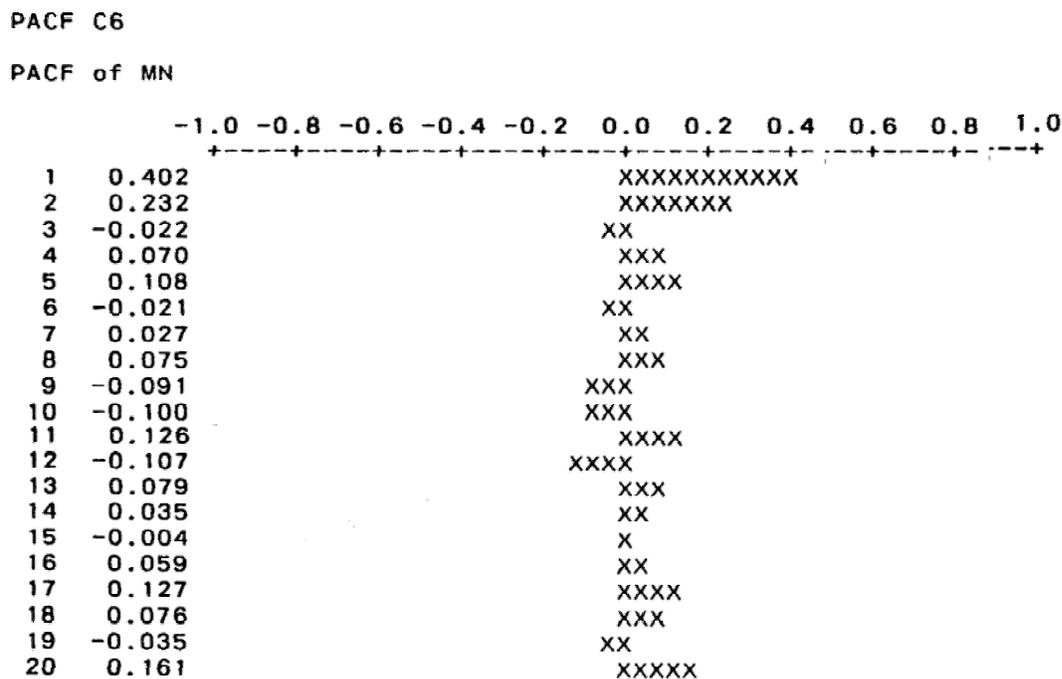


Figure 8.4k: Autocorrelation Function of Sulfate

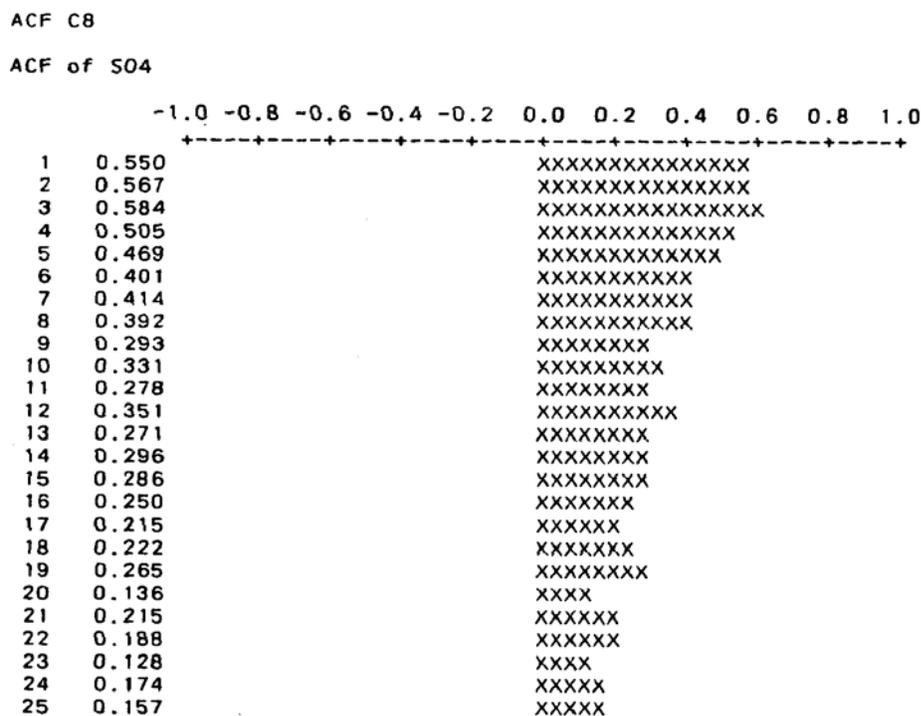
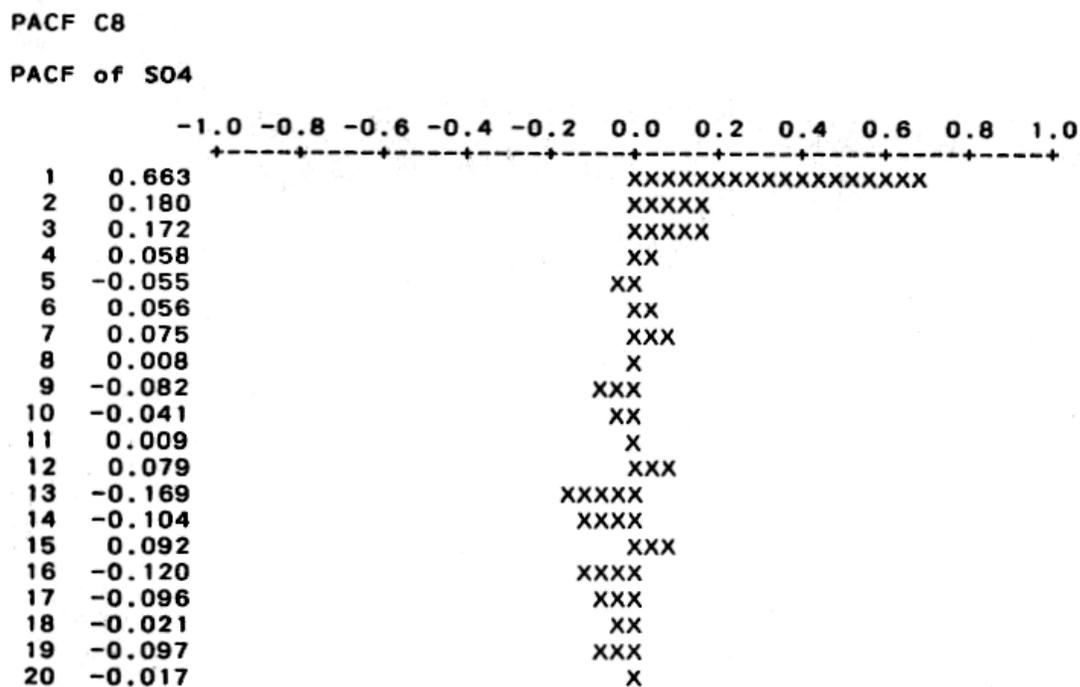


Figure 8.41: Partial Autocorrelation Function of Sulfate



Model Fitting to Selected Variables

Since many of the parameters show similar types of variation in terms of their Acf and Pacf representations, only some parameters were submitted to full time series analysis. The outcomes are summarized in Tables 8.8 and 8.9. Table 8.8 summarizes the tests performed on each model fitted to each parameter. Table 8.9 presents the models as equations relating values at time t to previous values of the parameters or its associated shock term (random error term, i.e., a_{t-1}).

There are only 107 observations of flow, and although first differences are indicated by the steep and steady decline of the Acf and the single large spike at lag 1 in the Pacf, it was decided to try an AR (1) model to determine whether the AR coefficient $\hat{\Phi}_1$ was an adequate proxy for the first difference. When an AR (1) was fitted to this variable, both $\hat{\Phi}_1$ and the mean were independent (see $r = 0$ in No. 1, Table 8.8). The chi-squared value has a probability between 0.20 and 0.10 of not being different from white noise. There were many spikes left in the Acf of the residuals but an AR (1) would suffice as a first approximation. It seems likely that the MA (0,1,1) would be a superior model.

Two models were fitted to the variation in pH. The first was an AR (1,0,0) model. While parameter estimates were independent ($r = 0$, No. 2, Table 8.8), the chi-square of the Acf of the residuals was significantly different from white noise. There was only one significant spike at lag 3. The second model was an AR (1,1,1) which could more adequately represent variation in

pH. The AR and MA coefficients were not, however, independent ($r = 0.64$, No. 3 in Table 8.8). The residual Acf yielded a chi-square value that is not significantly different from that of white noise. This model is indeed adequate to represent the series and there were no significant spikes in the Acf or Pacf of the residuals. The residual standard deviation showed a small improvement over the original standard deviation of the series (0.140 and 0.139 versus 0.151, see Table 8.8).

Table 8.8: Tests of the Different Models for Each Parameter

N	Parameter	Model	r^a	Chi-sq	d.f.	P	Spike	Standard Deviation	
								Resid.	Original
1.	Flow	AR (1,0,0)	0	29.16	22	$0.20 > P > 0.10$	many	630.43	931.14
2.	pH	AR (1,0,0)	0	34.85	22	$0.05 > P > 0.02$	1@3	0.140	0.151
3.	pH	AR/MA (1,1,1)	0.64	25.11	22	$0.30 > P > 0.20$	none	0.139	
4.	Iron	MA (0,1,1)	0	17.17	23	$0.90 > P > 0.80$	none	8.069	13.026
5.	Iron	AR (1,1,0)	0	27.68	23	$0.30 > P > 0.20$	1@2	8.349	
6.	Mn	MA (0,0,1)	0	38.27	26	$0.02 > P > 0.01$	1@2	0.902	0.835
7.	Mn	AR (1,0,0)	0	28.44	22	$0.20 > P > 0.10$	1@2	0.875	
8.	Mn	MA (0,1,1)	0	30.79	23	$0.20 > P > 0.10$	1@10	0.721	
9.	SO ₄	MA (0,1,1)	0	41.05	23	$0.02 > P > 0.01$	@3,6,9,12	33.01	44.85
10.	SO ₄	AR (1,0,0)	0	108.09	22	<0.001	@1,2,3+	36.96	
11.	SO ₄	AR (1,0,0)	[3] ^b	89.70	23	<0.001	many	46.90	
12.	SO ₄	AR (1,1,0)	88 ^c	32.72	21	$0.05 > P > 0.02$	@6,9	32.83	
13.	SO ₄	AR (2,1,1)	> 0.7 ^d	32.85	21	$0.05 > P > 0.02$	@6,9,12	32.72	44.85

- a. Correlation among the parameter estimates.
- b. This [3] = a seasonal @ lag 3.
- c. $r_{12} = 0.88$; $r_{13} = 0.4$; $r_{23} = -0.24$
- d. All coefficients highly positively correlated (i.e., redundant). >0.7

Acidity was considered to be sufficiently similar to pH and for this reason, not require any special testing from the Acf and Pacf of the original series. From the Acf and Pacf and from previous model fitting, an AR (1,1,1) or the MA (0,1,1) would be likely to adequately represent this variable.

Iron showed the same steep decline as flow as well as the same large spike at lag 1 in the Pacf. For this reason, two models were fitted to variation in this parameter. The MA (0,1,1) easily met all tests (see No. 4 in Table 8.8) and is an adequate representative model. The AR (1,1,0) met most of the tests, but not as successfully (see probability for chi-square, No. 5, Table 8.8). There also remained a significant spike at lag 2 in both the Acf and Pacf of the residuals from fitting the AR model. There was a large reduction in the standard deviation compared with its value in regards to the original series (see No. 4, Table 8.8). Ferrous iron was not analyzed because it resembled total iron so closely that similar results would be expected.

Manganese appears to possess a mixture of the characteristics of iron and pH in its Acf and Pacf. For this reason, three models were tried. The simple MA (0,0,1) was not adequate in terms of the chi-square value of the Acf of the residuals (No. 6, Table 8.8). It also possessed a significant spike at lag 2. When a simple AR (1,0,0) model was used, the chi-square of the residuals was not significantly different from that of white noise and the standard deviation of the residuals was reduced from that of the simple MA. There was still a significant spike at lag 2 in both the Acf and Pacf of the residuals.

As a check, a simple MA (0,0,1) was fitted to the first differences of manganese (i.e., an MA (0,1,1)). The results were similar, although the spike at lag 2 disappeared and a weak spike appeared at lag 10. This was determined to be too far along the Acf to be ignored. The standard deviation of the residuals was much improved 0.721 (No. 8, Table 8.8); over 76% improvement over the original series (Table 8.1 wherein the standard deviation is 0.9498 from $N = 107$).

Sulfate also showed a mixture of types in its Acf and Pacf and for this reason, was explored at greater length; first the MA (0,1,1) was fitted because this model appears to fit many cases in previous reports. The chi-square of the residuals was significantly different from that of white noise. There were many spikes in the Acf and Pacf at lags 3, 6, 9, and 12 implying a seasonal repetition. Next, an AR (1,0,0) was fitted to see how much of the trend shown by the large spike at lag 1 in the Pacf, could be reduced (No. 10, Table 8.8). The chi-square value was very large ($P < 0.001$) and there were many spikes at various lags in the Acf and Pacf of the residuals.

The next model applied was an AR (1,0,0) with a seasonal three term. This model proved ineffective because the chi-square value of the residuals remained very large (probability < 0.001 see No. 11, Table 8.8). The next step was to apply AR (1,1,0) with a seasonal AR of lag 2. Lag 2 of the first differences is equivalent to lag 3 in the original series (No. 12 in Table 8.8). This result was a strong improvement in the value of chi-square, but was still significantly different from that of white noise ($0.05 > P > 0.02$); the Acf and Pacf possessed spikes at lags 6 and 9. Finally, an AR (2,1,1) was applied and all the coefficients ($\hat{\Phi}_1$, $\hat{\Phi}_2$, $\hat{\Phi}_3$) were highly correlated and showed strong redundancies (No. 13, Table 8.8). The chi-square was essentially the same as in the previous model and possessed significantly large spikes at 6, 9 and 12.

It is important at this stage, to examine what the results of these models mean in terms of equations. When a suitable model is found, the coefficients should have some implications of substantive value. In most cases, a simple model possessing an equation that is easy to interpret is adequate. An AR (1,0,0) such as that for flow or pH is an example. As the models become more complicated, interpretation of the equations becomes more difficult. Unless there are definite reasons that a more comprehensive model would be appropriate, it is prudent to use a reasonably simple model.

The equations for the models used in Table 8.8 are summarized in Table 8.9. The first eleven equations are relatively simple. The last two equations, however, are obviously complicated, and it was decided to stop the analysis at this stage. It is suspected that the simple AR or MA models of the first differences are sufficient to represent most of the parameters. However, a seasonal model of some kind is required for sulfate. From the Acf and Pacf of the original

series, an AR model of first differences is likely to be most parsimonious. It will require an additional seasonal term (possibly an AR at lag 3) to remove the remaining significant spikes.

Table 8.9: Model Equations for the Variables (see Table 8.8)

No.	Variable	Equation
1.	Flow AR(1)	$Z_t = 0.742 Z_{t-1} + 1487.2 + a_t$
2.	pH AR (1)	$Z_t = 0.372 Z_{t-1} + 3.235 + a_t$
3.	pH AR/MA (1,1,1)	$Z_t = 1.121 Z_{t-1} - 0.121 Z_{t-2} - 0.808a_{t-1}$
4.	Iron MA (0,1,1)	$Z_t = Z_{t-1} + a_t - 0.525a_{t-1}$
5.	Iron AR (1,1,0)	$Z_t = .629 Z_{t-1} + 0.371_{t-2} + a_t$
6.	Mn MA (0,0,1)	$Z_t = 4.90 + a_t + .270 a_{t-1}$
7.	Mn AR (1,0,0)	$Z_t = 0.404 Z_{t-1} + 4.913 + a_t$
8.	Mn MA (0,1,1)	$Z_t = Z_{t-1} + a_t + 0.611 a_{t-1}$
9.	SO ₄ MA (0,1,1)	$Z_t = Z_{t-1} + a_t + 0.725 a_{t-1}$
10.	SO ₄ AR (1,0,0)	$Z_t = 0.550 Z_{t-1} + 296.9 + a_t$
11.	SO ₄ AR (1,0,0)	$Z_t = 0.572 Z_{t-1} + a_t$
12.	SO ₄ AR (1,1,0) (2,0,0)	$Z_t = 1.118 Z_{t-1} - 0.941 Z_{t-2} - 1.281 Z_{t-3} - 0.153z_{t-4} + a_t$
13.	SO ₄ AR/MA (2,1,1)	$Z_t = 1.380 Z_{t-1} + .188 Z_{t-2} + .182 Z_{t-3} + a_t - 0.424 a_{t-1}$

Summary

The first important characteristic of the variables from the Markson site is the lack of wide variation except in the flow variable. The second characteristic is the lack of any strong relationships between pairs of variables. The only high r values are the expected correlations between iron and ferrous iron, flow and ferrous iron, and flow and iron. The iron ferrous iron association is positive, whereas with flow, both are negative (i.e., high flows may lead to dilution of iron). The most striking feature of the time series graphs is the high flow over the period of February 1986 to July 1986, particularly because the flow is in logs. In general, this does not show up in any other variable. There are two very peculiar features which should be emphasized. First, there does not appear to be any reflection of this high flow event in most of the other variables (iron and ferrous iron are exceptions); second, pH shows no relationship to acidity or sulfate.

The most appropriate time series models require a first difference to remove any trend. For many cases, this may be adequately accomplished by an AR (1) term in the models. The residual, after fitting this kind of model, is a close approximation to white noise (i.e., random variation). The residual could, in most cases, be modeled fairly adequately by the usual MA (0,1,1) moving average model. This implies that once the trend is removed, the remaining variation is similar to a random walk. This could account for whatever relationships there are

between the variables, and suggests that linear correlation is not adequate to evaluate the relationships that do exist between the variables. The trend could well be due to the extreme event in the flow variable.

Sulfate however, does appear to show some possible indications of a seasonal pattern. It seems to possess some irregularities which go beyond the “random walk” type of residual. A number of models were tried in this case but none did any better than the MA. Nevertheless, there were many spikes in the Acf of the residual from the first differenced series at what appear to be regular intervals of lags 3, 6, 9, and 12. This implies a seasonal structure at three period intervals (which is a four period interval in the original series). The more complex models failed one or more of the test criteria and rather than complicate the issue further, the analysis was terminated.

Chapter 9: Statistical Summary and Review of Quality Control Limits

Establishment of baseline pollution loads for a coal remining permit requires proper sampling and chemical analysis of pre-existing abandoned mine discharges, and the appropriate statistical analysis of flow, water quality, and pollution load data. The term “proper sampling” is taken in two contexts: (1) collection and analysis of surface water and groundwater samples, including field measurements of flow and water quality parameters, sample preservation, transportation and storage, and chemical analyses, and (2) collection of a sufficient number of samples with sampling period duration and intervals that adequately represent the variations in flow and water quality throughout the water year. Abundant scientific literature exists on collection and analytical procedures for water samples. Guidelines and protocols for water sample collection from EPA, the U.S. Geological Survey (USGS) and other sources are compiled in Table 9.1, and are discussed briefly in Chapter 1.

Table 9.1: Guidance and Protocols For Water Sample Collection

#	Type of Resource	Title	Source	HTML
1	Field Procedures	National Field Manual for the Collection of Water Quality Data	USGS	http://h2o.usgs.gov/owq/Fieldprocedures.html
2	Field Operations Manual	EMAP Surface Waters Field Operations Manual for Lakes: June, 1997 EPA/620/R-97/001	EPA	http://www.epa.gov/emjulte/html/pubs/docs/surfwatr/97fopsman.htm
3	Monitoring Guidance	Office of Water NEP Monitoring Guidance EPA-842-B-92-004	EPA	http://www.epa.gov/OWOW/estuaries/guidance/
4	Procedures	Procedures for Handling and Chemical Analysis of Sediment and Water Samples. EPA/CD-81-1	EPA/ US Army Corps of Engineers	http://www.epa.gov/owgwwtr1/info/PubList/monitoring/docs/027.pdf
5	Protocols	National Water-Quality Assessment (NAWQA) Method and Guideline Protocols	USGS	http://wwwrvares.er.usgs.gov/nawqa/protocols/doc_list.html
6	Sampling	Ground Water Sampling EPA: A Workshop Summary Nov. 30- Dec. 2, 1993. EPA/600/R-94/205	EPA	http://www.epa.gov/swrust1/cat/gwworkshop.pdf
7	Techniques	Publications on Techniques of Water Resource Investigations	USGS	http://water.usgs.gov/owq/FieldManual/chapter1/twri.html
8	Sample Preservation	Fixing Water Samples Bureau of Mines and Reclamation ID# 562-3200-203 May 1, 1997	EPA/ Bureau of Mining and Reclamation	http://www.dep.state.pa.us/dep/subject/All_Final_Technical_guidance/bmr/562-3200-203.htm

#	Type of Resource	Title	Source	HTML
9	Sampling	Quality-control design for surface-water sampling in the National Water-Quality Assessment program (USGS Open File Report 97-223)	USGS	http://wwwrvares.er.usgs.gov/nawqa/protocols/doc_list.html
10	Sampling	Ground-Water Data-Collection Protocols and Procedures for the National Water-Quality Assessment Program: Collection and Documentation of Water-Quality Samples and Related Data (USGS Open-File Report 95-399)	USGS	http://wwwrvares.er.usgs.gov/nawqa/protocols/doc_list.html
11	Sampling	Field Guide to Collecting and processing samples of stream-water samples for the National-Water Quality Assessment program (USGS Open File Report 94-458)	USGS	http://wwwrvares.er.usgs.gov/nawqa/protocols/doc_list.html

Most of this report and EPA's *Coal Remining Statistical Support Document* (EPA-821-B-00-001) are devoted to discussion of the second context (sample period duration and interval) of proper sampling of pre-existing discharges and to the associated statistical analyses of the sample data.

The baseline pollution load is essentially a statistical summary of a data set generally consisting of 12 or more samples collected prior to issuance of a remining permit. Chapter 2 of this report provides an overview and explanation of exploratory and confirmatory statistical methods that may be used in establishing the baseline pollution load. The fundamentals of univariate, bivariate, multivariate, and time-series statistical analyses also are outlined in Chapter 2. The algorithm for analysis of mine drainage discharge data (see Figure 3.1) developed in 1987 by Dr. J.C. Griffiths and other authors of this report is described step by step in Chapter 3, and also is included in Chapter 1 of the *Coal Remining Statistical Support Document*. This algorithm was used in conducting the univariate, bivariate and time series analyses of the six relatively long term mine drainage data sets described in Chapters 4 through 8 and Appendices A through F of this report. Chapter 5 of the *Coal Remining Statistical Support Document* contains an additional 10-20 years of data on some of these six sites including data collected prior to, during, and post-remining.

The sampling plan, data collection/organization and statistical analysis components of establishing the baseline pollution load should be integrated in a continuous process. In general, abandoned mine discharges flow continuously, thus, it should not be difficult to collect an adequate number of samples. However, these discharges frequently exhibit significant variations in flow and water quality, and logistical problems may be encountered in attempting to capture

the full range and distribution of seasonal variations. Ideally, there are no missing data, and a sufficient number of samples are collected throughout the water year, at equal sampling intervals that are small enough to capture the range of natural seasonal variations. Continuous flow recorders and automated water quality samplers may be part of that ideal world, but they are rarely available or justifiable for use in remining permitting activities. Typically in routine remining permit sampling, adjustments must be made in data organization and analysis to account for missing data, unequal sampling intervals, data that are not normally distributed or that lack expression of the true extremes, and other problems.

This chapter summarizes the findings of the statistical analyses of abandoned mine discharge data contained in Chapters 4 through 8 and Appendices A through F of this report. This summary includes examples of sampling plans, data organization, univariate analysis, bivariate analysis and time series analysis, with emphasis on the practical applications of the time series. The chapter concludes with a review of the use of quality control limits for establishing and monitoring baseline pollution load at remining sites.

Sampling

The sampling plan is critical in all statistical studies and is one of the most difficult problems to resolve. One problem is the usual compromise between the samples one would like to collect and the cost of collecting them. From a research point of view, to perform a time series analysis that correctly models the variation of a parameter (e.g., flow), it is necessary to obtain observations over several years so that the model becomes truly representative. Such large collections of data are rare and the six long term data sets presented in this report are both atypical and best-case scenarios.

Another requirement that is critical for time series analysis is that the samples should be collected at equal time intervals. This criterion is almost impossible to achieve in routine sampling practice. For example, when an extreme event occurs, it is usually for at most a few days, and the common sampling intervals of one week, two weeks, or one month could easily miss the event. Secondly, if the event is a heavy snowfall or a flood, it may be physically impossible to access the sample location. The data analyzed for the studies presented in this report address these problems and other causes of unequal intervals and missing or erroneous data (e.g., loss of sample, incorrect data entry).

It is advisable to establish a sampling plan that recognizes these difficulties. It is also essential to examine the data in detail, as described in the earlier chapters of this report. It should be recognized that because of the nature of a typical data set, a rigorous statistical analysis must not be taken too far; one must compromise by being as accurate as possible without requiring impossible precision. (It is, theoretically, always possible to measure the degree of precision by replicate sampling although, in practice, replicate sampling may be too costly). The following guidelines are, therefore, a compromise and are presented as recommended guidelines only.

Sampling should be representative, cover a period of at least one year, and include both high and low flow periods within that year. Suppose 12 samples are taken at a rate of one per month for a

year. This scenario may not adequately represent baseline conditions because local extreme storm events typically occur within a few days and can result in a great range in variability between monthly samples. Extreme events are often missed with this sampling arrangement.

One recommendation for representative sample collection within the Appalachian Basin would be to use stratified sampling; divide the year into three periods of about equal length, arranged to cover high and low flow periods as follows:

January – March	April – June	September – November
high flow	intermediate flow	low flow
90 days (91 days during leap year)	91 days	91 days

The months of July, August, and December are eliminated from this recommended scenario because these months typically don't include extremes and include events covered during the other three periods. Taking one sample every 15 days within each of the three intervals would equal a total of 18 samples. Of course, to determine initial baseline pollution loading, it is preferable to increase the number of sample intervals and to extend the sampling period for more than a single year.

Data Preparation and Organization

It is always advisable to examine raw data before submitting it to analysis. The presence of unusual values and missing data usually require some kind of action. These and other features of the data set are best examined by graphical procedure. A graph of discharge or log discharge in gallons per minute versus days can be very helpful in identifying data gaps and unusual values (e.g., Figure 9.1).

Figure 9.1: Example Graph Log Discharge versus Days (Also Figure 4.2)

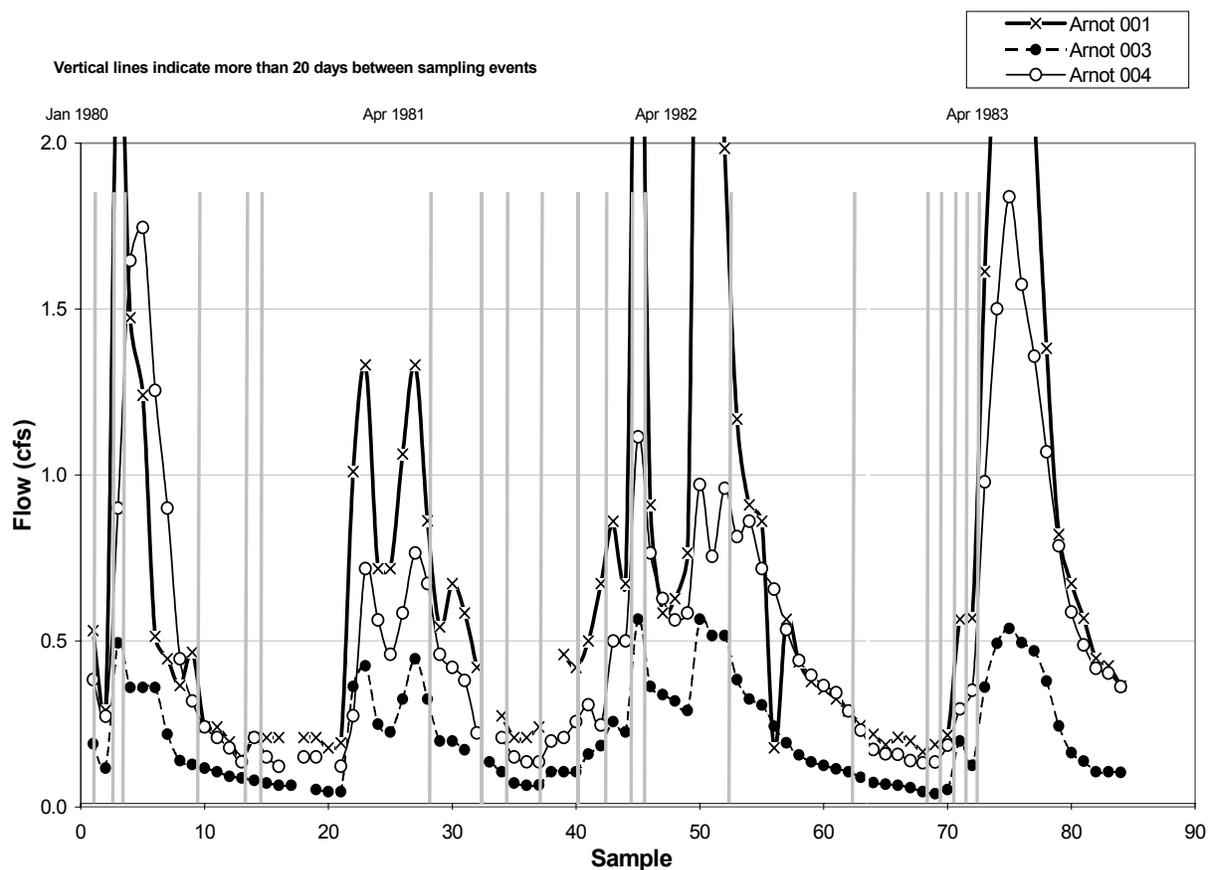


Figure 9.1 can be used to observe two kinds of information:

- 1) Missing values. The distribution of missing values is critical to more sophisticated analysis (particularly, time series). In general, a few missing values are not very serious, but if there are many and if they occur in clusters (Figure 9.1), the omissions may make further analysis very inexact.

Missing values frequently occur during extreme events because during these events, sample sites are difficult to access. Sometimes, if the missing values are few and widely distributed, they may be replaced by the means (if the frequency distribution of the data is reasonably symmetrical), or by the median (if the frequency distribution of data is extremely skewed).

In Chapters 7 and 8, a frequency distribution of the first differences between days of observation was constructed. Once constructed, both the number and the concentration density of missing observations was clearly displayed as the frequency of intervals of different lengths between observations. The variation for the Fisher site is from one day (difference = 0) to an interval of 104. The mean (26.7 days) is very nearly equal to the

median (26.5 days), thus, the distribution is roughly symmetrical around the expected sampling interval of 28 days. The central 50 percent of the distribution ($Q_1 - Q_3$) lies between 12.3 and 33 days. The most serious discrepancies are, however, that there are five observations between 70 and 104 days (four of these are 90 days or more). These large gaps in the data preclude rigorous time series analysis which requires a very close approximation to equal intervals between observations.

- 2) Extreme Values. The second kind of preliminary observation is to examine the data for extreme values (usually on the high side). Again, the distribution of extremes is important. Prior to examination of this data, it was believed that extreme flows would occur at regular seasonal intervals, for example, during the Spring melt. However, examination of the data presented in Figure 4.2 shows that extreme events were spread over periods from February to April (for Spring melts) and from May through June (for intense summer rains, often as thunderstorms). These wide spreads of extreme events, together with missing data (which often occurred during extreme events), made it very difficult to detect any expected true seasonal effects.

One further point concerning extremes, is the fact that these extremes tend to introduce strong skewness (asymmetry) into the frequency distribution. This skewness is usually positive (i.e., extreme values are at the high end of the data distribution). It is conventional to apply a transformation to reduce this skewness, and logarithmic transformation is usually the most effective. It is sometimes questionable, however, to what extent the effects of extreme events should be suppressed if at all. Thus, it is prudent to examine the raw data very carefully to decide whether transformation is appropriate.

Another effect of expressing variables in logs instead of concentration is shown in Figure 4.8, where manganese (mg/L) is plotted against log transformed discharge (cubic feet per second, cfs). There is an obvious linear association between the two variables. If discharge is expressed arithmetically in cfs (see Figure 4.9), the association is curvilinear. However, there is still a strong association between the variables. Note also that there are several outliers that appear to deviate from the trend. Expression of the log transformed data tends to suppress the effects of extreme outliers.

Univariate Analysis

The main features of the univariate statistical analyses described in Chapters 4 through 8 are the frequency distributions of the water quality parameters and flow measurement data, and the tables of summary statistics (e.g., Tables 4.1, 5.1, 6.1, 7.2, and 8.2). These tables typically include the following summary statistics: number of observations (N), number of missing observations (N*), mean, median, 10 % trimmed mean, standard deviation, standard error of the mean, minimum and maximum values (i.e., range) and quartiles. Several of these summary statistics are included in Table 1.2a of EPA's *Coal Remining Statistical Support Document* and are incorporated as conditions of remining permits (i.e., median, range, and quartiles).

An additional statistic, the coefficient of variation (CV) is included in the tables in Chapters 4-8. The coefficient of variation, usually expressed in percent (CV%), is defined as the ratio of the standard deviation to the mean multiplied by 100. This is a useful approximate guide to the degree of variation in a parameter. In general, a $CV < 30\%$ represents a stable, in control variable. In Chapters 4 through 8, most of the parameters showed much larger variation, principally because of the effects of extreme events. Use of the coefficient of variation with log transformed data may result in extreme distortion because the transformation leads to a mean of small value, resulting in a divisor of the ratio that is small and thus a CV that is inflated.

In Chapters 4 through 8, the frequency distributions of many water quality and pollution load variables were found to be normally distributed, or at least symmetrically distributed, around a value of central tendency (see for example, Figures 4.5 and 8.1e). Numerous other variables had frequency distributions that exhibited positive skewness. In Figure 5.3a, for example, there are two single observations for discharge at 50 and 80-85 gallons per minute which represent extreme events in flow. These values introduce a strong positive skewness in the histogram towards high values. In Figure 5.3b, discharge is transformed to log flow and the skewness is now towards the negative side (i.e., the transformation has over-corrected for positive skewness). In such cases, it is best not to log transform the data. Acidity (mg/L, Figure 5.4a) is somewhat symmetrical and, as would be expected, log transformation introduces a strong negative skewness (Figure 5.4b). Again, no transformation should be used.

It is possible of course, to use a less pronounced transformation (such as the square root of the variable) that may avoid the over-correction that can result from logarithmic transformation. The use of various transformations is reviewed by Tukey (1977, Chapter 3), Velleman and Hoaglin (1981, p. 46-49), and Box and Cox (1964).

Bivariate Analysis

Bivariate analysis is used to examine the relationship between pairs of variables. One expects, for example, pH and acidity or sulfate to be inversely related (as acidity increases pH declines). In the case of calcium and manganese, on the other hand, one expects positive correlation (both either increase or decrease together). The correlation coefficient (r) is used to represent the (linear) relationship between any pair of variables. The coefficient of determination (r^2), however, is a better measure of the intensity of the association between a pair of variables. For example, an $r = 0.7$ seems large because the range of r is from -1 to $+1$. However, $r = 0.7$ means that $r^2 = 0.49$, or that there is 49% in common between the two variables, with 51% of the variation “unexplained” by the association. For example, it would be necessary to have an $r > 0.8$ (i.e., $> 64\%$ in common) to claim that a strong association exists. (See Chapter 8 for additional discussion)

Another feature that can be evaluated using r and r^2 is the statistical test that accompanies a specific value of r . For example, the probability statement that for a sample size of $N = 174$ (see Chapter 6), a value of $r > 0.124$ is significantly different from zero at the 5 percent probability level, should be accompanied by the corresponding value of r^2 . In Table 6.3, the correlation coefficient between pH and acidity ($r = -0.365$) comfortably exceeds the $r (+/-) 0.124$, thus, it is

statistically significant. Nevertheless, the corresponding $r^2 = 0.133$ indicates that only 13.3% of the variation is common to both variables.

Bivariate analysis of the Ernest site data also showed a strong association between all pairs of the load variables ($r^2 > 80\%$, see Figures 6.5a, b, and c). This clearly suggests that because discharge is used as a common factor in converting concentration to load, it tends to overwhelm the relationships among the other variables. This problem with pollution load variables also was detected in the analysis of data from the other sites described in Chapters 4 through 8.

In Figures 6.5a and 6.5c, the variation between the parameters increases as their values increase. This phenomenon is called heteroscedasticity and, in general, it is advisable to plot the logs of the values to make them homoscedastic. Since heteroscedastic parameters show a difference in variability with change in values, no probability statement should be made without transformation to make the variables homoscedastic. Peculiarly, the change from heteroscedasticity to homoscedasticity does not lead to a major change in the value of r . However, it does make the probability statements more reliable.

One more avenue was explored during bivariate analyses in Chapters 4 through 8, and that was to determine whether there is any lag in association between parameter pairs. The cross-correlation function is used for this purpose. The cross-correlation function calculates the linear association between observations 0 to t days apart, and thus gives an indication of when the association is strongest. The range of t is from $-\{\sqrt{N} + 10\}$ to $\{\sqrt{N} + 10\}$, where N is the number of observations in the series. For example, if an event occurs that affects one parameter immediately and affects another parameter five observations later, the linear correlation coefficient may be quite low at zero lag but may show a strong association after a five day lag.

Bivariate statistical analysis of data from the Fisher site (Chapter 7) can be used as an example of the use of the cross-correlation function. The correlation coefficients of zero order for each pair of variables are given in Table 7.3. The zero order value of $r = 0.663$ for acid versus iron was the highest correlation between any of the water quality parameters. The zero order correlation coefficient for iron and manganese is $r = 0.396$, and this is the maximum value. The maximum correlation coefficients and corresponding lag values from the cross-correlation functions are summarized in Table 7.4. Few are meaningful, and most are barely significant. This indicates that the degree of association was correctly represented for these variables by their conventional zero order correlation coefficients (Table 7.3).

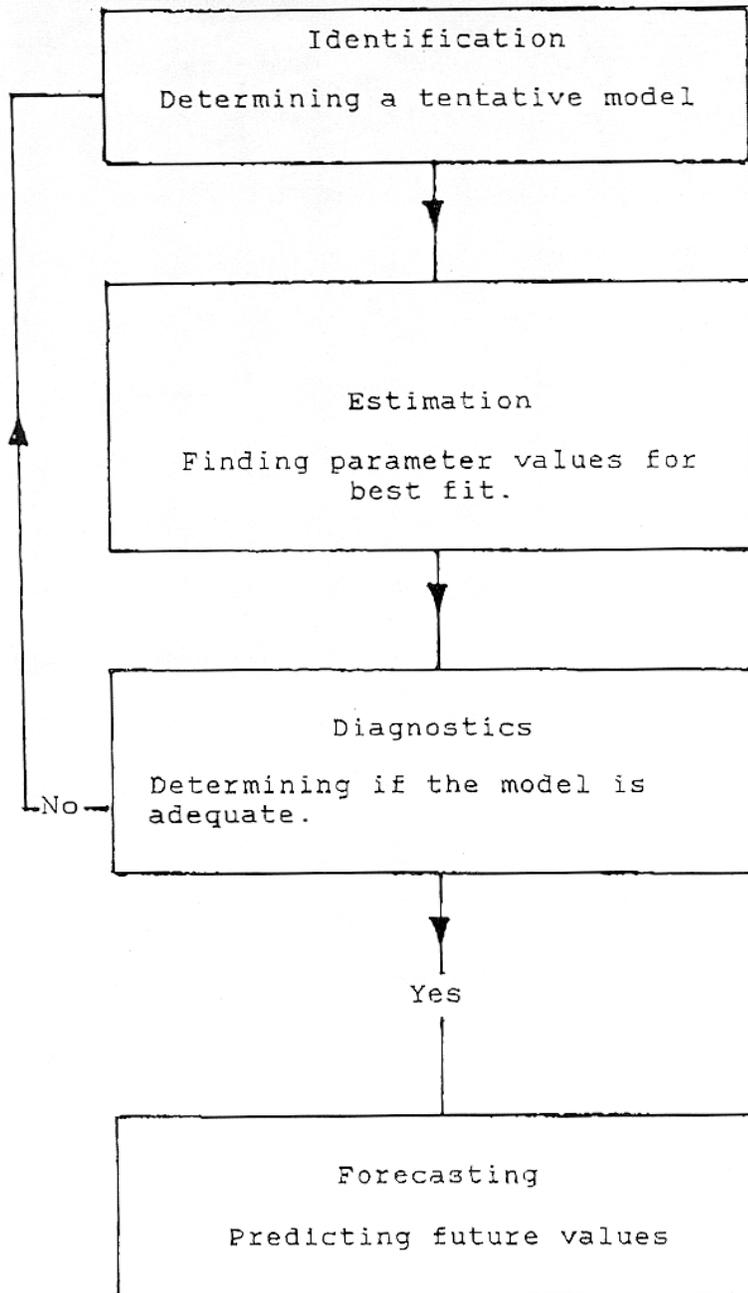
Time Series Analysis

There are two fundamental aspects to the time series analyses described in Chapters 4 through 8 and Appendix A:

- 1) use of a simple time series plot of the data for a particular water quality or flow variable, with or without quality control limits, to assist in evaluating patterns of variation through time (essentially an exploratory data analysis step), and

2) application of the full Box-Jenkins time series analysis and model building procedures (see Figure 9.2).

Figure 9.2: Flow Chart for Box-Jenkins Time Series Analysis



Time series analysis begins with a plot of the observations against time (days or dates). This plot is a simple outcome and can give helpful guidance to the type of time series that is represented by the variation in the data. Furthermore, the quality control limits, either some suitable multiple of (2 or 3 times) the standard deviation or, in this report, a non-parametric substitute for the standard deviation (e.g., confidence intervals around the median):

$$= Md \pm 1.96 [1.25 R / (1.35 \sqrt{N'})]$$

Where, R = the Interquartile Range (after McGill, R., et al., 1978).

With this application, outliers plotting beyond the confidence limits are easily seen, and the arrangement of the outliers may be either irregular (occurring as unique individuals) or systematic (e.g., periodic). Examples are given in Figure(s) 8.3.

When the plotting procedure is complete, analysis may continue using standard Box-Jenkins Time Series modeling. There is also an exhaustive Box-Jenkins procedure may be applied if there is a suitable computer package available. The main advantage of the exhaustive Box-Jenkins analysis is that very thorough testing may be performed as an automatic procedure at each stage in the analysis. The exhaustive procedure is described in many textbooks (e.g., Box and Jenkins, 1970, Nelson, 1973, and Vandaele, 1983) and the package of computer programs for pursuing the step by step analysis is also readily available in many computer systems programs (e.g., Dixon's BMDP Manuals (after 1980)).

A flow chart for Box-Jenkins time series analysis is provided in Figure 9.1. The first step is to identify a tentative model and to improve on the model by iteration through the procedure, until a more satisfactory model is found. The global model is called an ARIMA model or an Autoregressive Integrated Moving Average Model. This family of models may be summarized for convenience as an AR (autoregressive) or MA (moving average) model. A back-operator is defined as $Bz_t = z_{t-1}$ where z_t is the set of observations taken at various equally-spaced values of t (time). An autoregressive model may be represented as AR (1,0,0) which stands for an autoregressive model of order (1) with no differences (0) and no moving average terms (0); an analogous series is the MA (0,0,1). This permits extensions to AR (2), ARI (2,1,0) etc. and similarly for the MA models MA (2), IMA (0,1,2) etc. Seasonal models may be included as, for example, an ARIMA (1,1,1) (1,0,1), which represents a first order ARIMA model, together with first order seasonal autoregressive and moving average terms (Box and Jenkins, 1970, p. 322).

The basis for identification of a suitable model is the autocorrelation function (Acf) and the partial autocorrelation function (Pacf) of the observations. It is assumed that the series is stationary (i.e., the observations are free of trend). If a trend is present, it is typical to take first differences of the observations and to analyze z_{t-1} instead of z_t . In practice, it is rare to require second differences, but they are available if needed. This is where the back-operator ($Bz_t = z_{t-1}$) is useful and is why a differenced series is called integrated. The form of the Acf and Pacf is usually adequate to determine an appropriate model and one may then proceed to the estimation stage.

The variables flow, acidity and acid-load from the Ernest Refuse Pile data were chosen as examples of the use of Acf and Pacf in selecting a preliminary model. Flow shows a steady, almost straight line decline in Acf values over the first 15 lags, implying the presence of a strong trend (Figure 6.8c). This is confirmed by the corresponding Pacf which consists of a large overwhelming spike at lag 1 (Figure 6.8d). It is advisable to take first differences to remove the effect of the trend. After differencing, a first order MA (0,1,1) fits the series adequately.

The Acf for variation in log transformed acidity is entirely different in appearance, possesses at least three significant peaks at lags 1, 2, 3, and is otherwise reasonably featureless (Figure 6.8e). The corresponding Pacf shows only two spikes at lags 1 and 2 (Figure 6.8f). An MA (0,1,2) model was tried and found to be over-identified (i.e., possessed too many coefficients). For this reason an MA (0,0,2) was fitted and found adequate.

When log transformed acid-load was examined, the Acf and Pacf were almost identical to their equivalents for flow (compare Figures 6.8 c and d with 6.8 g and h). There is little doubt that flow dominates the variation when the variable is converted from concentration to load using flow as the divisor.

After complete analysis using a variety of models, it was concluded that the first order MA (0,1,1) was the most parsimonious and appropriate model for the Ernest site, and showed no significant departures from what was expected after stringent testing. The form of the equation is: $z_t = a_t - 0.247 a_{t-1}$ with the coefficient $\hat{\theta}$ being from log acid load.

The Markson site data presented in Chapter 8 and Appendix F provides the best example of the full range of the Box-Jenkins time series analysis. The steps in the analytical procedure shown in Figure 9.1 are followed using sulfate data because it was one of the few parameters where a seasonal component appeared to be present (although never finally identified).

Identification of a tentative model was made through the Acf and Pacf of sulfate in Figures 8.4k and 8.4l. The MA (0,1,1) was chosen as a starting model because the Pacf had a single large spike (Figure 8.4l) and because this model was, in general, the most suitable for many other parameters at different sites. It was then necessary to test the residuals (i.e., the deviations of observed values from those of the fitted model). The Acf of the residuals yielded a chi-square of 41.05 with 23 degrees of freedom leading to a probability that a chi-square value as high as the one observed arising from white noise equals $0.01 < P < 0.02$. In other words, the chi-square is too large to be acceptable. The Acf of the residuals is summarized in Table 9.1. It can be seen that significant spikes occur at lags 3, 6, 9 (i.e., in a possible periodic recurrence usually shown by a seasonal type model). The interval of three observations in the first differences is likely to represent four in the original data, thus, the intervals are four weeks apart. If a difference of the residual is taken, the chi-square equals 145.93 with 23 degrees of freedom. Hence, the series is now over-differenced and only the differences of the initial series are required.

Table 9.2: Acf of the Residuals from Fitting an MA Model to the Original Observations After Taking a First Difference: SO₄

Lags 1-8	-0.07	0.04	0.13	0.02	-0.01	-0.12	0.00	0.01
Standard Error	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.07
Lags 9-16	-0.17	-0.03	-0.12	0.10	-0.07	0.01	0.05	-0.01
Standard Error	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07

Mean = -1.972; Standard Error = 2.076; N = 252

* Spikes beyond the 16th lag unlikely to be real. Chi-square = 41.05; 0.01 < P < 0.02; degrees of freedom = 23

The Pacf is also listed in Table 9.2 and the significant peaks (i.e., those beyond twice their standard error) are at 3, 6, 9, and 11 or 12. This again suggests a seasonal model. It should be noted that these spikes only slightly exceed their standard error thus, the seasonal effect, if present, is weak.

Table 9.3: Pacf of the Residuals from Fitting an MA Model to the Original Observations After Taking a First Difference: SO₄

Lags 1-8	-0.07	0.03	0.14	0.04	-0.02	-0.14	-0.03	0.03
Lags 9-16	-0.13	-0.05	-0.13	0.12	-0.03	0.03	-0.01	-0.02

2 Standard Error = $2 [1/\sqrt{252}] = 2(0.063) = 0.126$.

Examination of the residuals plotted against the date of observation shows no clear pattern of deviation. As can be seen in table 9.3, the significant residuals are arranged irregularly and occur prior to the 130th observation (out of 253 observations).

Table 9.4: Arrangement of Significant Deviations of the Residuals (> 2 Standard Error = 66.02)

Observation Numbers of Significant Residuals	
< Expected	> Expected
33	45
80	87, 90
104	103
122	121

Continuing with model fitting and diagnostic testing, the next step is to examine the estimators of the parameters. For an IMA (0,1,1), there are two estimators: the coefficient of the noise term a_{t-1} ($\hat{\theta} = 0.725$), and the overall residual standard deviation. Calculated 95% confidence limits for θ are 0.639 and 0.811, clearly confirming that the coefficient is real because the interval does not contain 0 or 1.

A number of potentially appropriate models were fitted to see if a suitable model could be found. The results of model fitting for the Markson site data are summarized at the bottom of Table 8.8). The best candidate was the IMA (0,1,1). All other models had notable failures of one or more diagnostic tests. This outcome implies that the first differences (z_{t-1}) of the original observations (z_t) represent a random walk. The seasonal effect appears to be too weak to show a positive response.

With the exception of the final step (forecasting or predicting future values), the time series examples from the Ernest and Markson sites discussed above provide a summary of the Box-Jenkins procedures listed in Figure 9.1. The last step was attempted using all the data sets presented in this report without great success. Results of this attempt using the Clarion site sulfate data are presented in Chapter 5. The reasons for this, described below, are characteristic of the six abandoned mine drainage data sets analyzed in this report.

Given the model, it is necessary to estimate the parameters for best fit. Diagnostics are applied to determine if the model is adequate and may also be used to compare different models to select the most appropriate. Finally, predictions or forecasts may be made of future values based on the selected model. This last step was shown to be of little value because extreme events inflated the confidence limits around the forecasts and thus, were not useful. There are many alternative extensions of the analytical time series procedure that can be followed, but because of extreme events, and because of difficulties with missing data and unequal values of t , it was considered imprudent to pursue the analysis further.

Quality Control Limits

The main objective of this study was to perform a statistical analysis (i.e., univariate, bivariate, and time series analyses) of numerous, long term abandoned mine drainage data sets in order to provide the foundation for developing and implementing a simple quality control approach for routine baseline pollution load analyses for remining permits. The six data sets included in Chapters 4 through 8 and Appendixes A through F of this report contain a greater number of samples (N) for a longer duration (and in some cases a tighter sampling interval) than typical remining permit baseline pollution load data sets. In addition, the statistical analyses in these chapters are more rigorous and exhaustive (see Figure 3.1) than intended for routine use in remining permits. However, much was learned from the statistical analyses of these six data sets (particularly the time series analyses) that can be applied to the use of quality control limits in establishing baseline pollution load and monitoring variations in the pollution load.

Two examples of the many variables in the six data sets are illustrated in Figures 8.3. Figure 8.3c indicates a variation in sulfate from the Markson site over a period of 253 days. Variation in total iron is shown over the same period in Figure 8.3d. As a guide to this “long range” variation, quality control limits are inserted in both graphs. One set of those limits consists of the conventional mean (\bar{X}) and the range between plus and minus two standard deviations ($\pm 2 \hat{\sigma}$). The second set is calculated around the median (Md) and Tukey’s recommended non-parametric limits:

$$\text{Md} \pm 1.96 [1.25 R / \{1.35 (\sqrt{N'})\}]$$

Where, R (H-Spread) = the interquartile ($Q_3 - Q_1$) range (described in McGill et al., 1978 and Velleman and Hoaglin, 1981, p. 79).

In Figure 8.3c, the sample size for the sigma limits (N') is one. However, for the non-parametric limits, the sample size is 12. Thus, the denominator becomes $1.35 \times \sqrt{N'} = 1.35 \times \sqrt{12} = 4.677$. These quality control limits are equivalent to confidence limits and are in common use in manufacturing. Quality control is maintained by choosing a sample size of, say 4, and then calculating the confidence limits around the mean of samples of size 4 which are

reduced from the single sample case by the $\frac{1}{\sqrt{4}} = 1/2$. This is, in turn, based on the relationship between the standard deviation of a single observation and the standard deviation of a mean with sample size 4 (i.e., the standard error of the $\hat{\sigma}_{\bar{x}}$ mean, as $\hat{\sigma}_{\bar{x}}$ follows (Griffiths, 1967, p.22):

$$\hat{\sigma}_{\bar{x}} = \hat{\sigma} / \sqrt{N'}$$

Where, $\hat{\sigma}_{\bar{x}}$ = the standard error of the mean.

By increasing the sample size, the confidence belts may be reduced to any desired (or affordable) limits. While this relationship holds, strictly speaking, only for a normal distribution, it is approximately true for nearly all symmetrical distributions and is substantially true for moderate departures in skewness or kurtosis.

A further series of options may be tailored to the particular problem at hand by adjusting the width of the confidence limits. In the examples discussed thus far, the limits were at the 95 percent probability level. In other words, using the range of two standard deviations, we include 95 out of every 100 observations and only 5 are expected to fall outside these limits. The same feature is approximately true of the non-parametric range. This range may be widened to 3 standard deviations, in which case about 3 observations in 1000 are expected outside the quality control limits.

In Figure 8.3c for sulfate, the two standard deviation limits emphasize the nature of the variation. Variation in sulfate starts out above the mean and above the upper confidence belt, but gradually declines with time until beyond observation number 135. Beyond observation 135, variation tends to remain within the confidence belts, and after the 230th observation, variation remains around the lower confidence belts. The quality control limits help to indicate this gradual decline despite the wide variation. The first 35 observations are persistently above the upper quality control limit, implying that some treatment of the discharge is necessary. Departures such as the 80th and 105th observations, on the other hand, are isolated events and no action is required.

The same features appear in the graph of total iron (Figure 8.3d). The earlier observations (to about 80) are mostly above the mean and around the upper quality control level. From 80 onwards, variation remains below the mean and is lowest beyond the 230th observation. In both graphs, there are some large gaps of missing observations.

In setting up baselines, and in subsequently using the baselines to judge the variation in any particular parameter, the sample size is always one so that only the conventional spread of two standard deviations and the equivalent spread measured by the interquartiles around the median are relevant. In this case the relationship: $Md \pm [1.96 \{1.25 R / (1.35 \sqrt{N'}\}]$ with $N' = 1$ reduces to $Md \pm (1.815R)$ and the calculations for sulfate and total iron are outlined in Table 8-7.

These calculations are presented to show the orders of magnitude of the different quality control limits. The rather large difference in the spreads around the mean and the median for ferrous iron (Tables 8.6 and 8.7), is essentially due to the strong negative skewness of the logs of ferrous iron. This example clearly shows that the non-parametric spread around the median is more suitable for these data. Little is lost if the distribution is symmetrical and much is gained if the data are either positively or negatively skewed.

Conclusions

The main objective of this study was to perform a statistical analysis (i.e., using univariate, bivariate, and time series approaches) of numerous, long term abandoned mine drainage data sets in order to provide the foundation for developing and implementing a simple quality control approach for routine baseline pollution load analyses for remining permits.

Sample Collection

Establishment of baseline pollution loads for a coal remining permit requires proper sampling and chemical analysis of pre-existing abandoned mine discharges, and the appropriate statistical analysis of flow, water quality, and pollution load data.

- The term proper sampling means the collection of a sufficient number of samples for a duration and at approximately constant intervals that adequately represent the variations in flow and water quality throughout the water year.

- Sampling should be representative, cover a period of at least one year, and include both high and low flow periods within that year.
- One recommendation for representative sample collection within the Appalachian Basin would be to use stratified sampling; divide the year into three periods of about equal length, arranged to cover high and low flow periods.

Discharge Variability

These pre-existing discharges frequently exhibit significant variations in flow and water quality, and logistical problems may be encountered in attempting to capture the full range and distribution of seasonal variations. There are two types of variation in pollution load that are of interest in evaluating monitoring data during and after remining to determine whether the variations are out of control compared to the established baseline conditions.

- The first and most obvious pattern of variation occurs when there are a series of extreme events, which consistently exceed the upper control level. This variation pattern indicates a sudden and dramatic increase in pollution load which may be attributed to remining, and which is referred to as the dramatic trigger.
- The second pattern of variation of concern is a trend of gradually increasing pollution load, where the general pattern of pollution load observations is increasing above the baseline central tendency value over time without exceeding the upper control level. As this second pattern of variation is much less dramatic than the first, and takes much more time and effort to detect, it is referred to as the subtle trigger. The reason that these two patterns of variation are referred to as triggers is that they can be used to initiate the requirement for a mine operator to treat a pre-existing discharge to a numeric effluent limit. If fair and reasonable consideration is given to the concerns of the mine operator and protection of the environment, the treatment triggers must be carefully established so that they are: (a) not set off prematurely or erroneously, adversely affecting the mine operator, or (b) set off too late resulting in additional mine drainage pollution without treatment.

Data Set - Initial Evaluation

The baseline pollution load is essentially a statistical summary of a data set generally consisting of 12 or more samples collected prior to issuance of a remining permit. In routine sampling for remining permits, adjustments must be made in data organization and analysis to account for missing data, unequal sampling intervals, and data that are not normally distributed or that lack expression of the true data extremes.

- It is always advisable to examine raw data before submitting it to statistical analysis. The presence of unusual values and missing data usually require some kind of action. A graph of concentration versus time or discharge or log discharge in gallons per minute versus days can be very helpful in identifying data gaps and unusual values. Missing values frequently occur during extreme events because during these events, sample sites are difficult to access.
- Another kind of preliminary evaluation is to examine the data for extreme values (usually on the high side). The wide spreads of extreme events, together with missing data (which often occur during extreme events) may make it very difficult to detect any expected true seasonal effects.

Univariate Analysis

- The main features of the univariate statistical analyses are the frequency distributions of the water quality parameters and flow measurement data, and the tables of summary statistics (e.g., Tables 4.1, 5.1, 6.2, 7.2 and 8.2).
- The frequency distribution is a graphical summary of the sample data. Its shape and accompanying summary statistics enable a greater understanding of how a parameter behaves. The normal distribution (shown in Figure 2.2) is the most widely known and most useful frequency distribution. It is also known as the bell-shaped curve.
- A major problem that is frequently encountered in the statistical analysis of water quality parameters is that the sample data are not normally distributed because it is typical to have many small valued observations in the data set and a few very large values representing extreme events. Extremes tend to introduce strong skewness (asymmetry) into the frequency distribution. This skewness is usually positive (i.e., extreme values are at the high end of the data distribution). It is conventional to apply a transformation, commonly logarithmic, to reduce this skewness (See Figure 5.3a). However, it is prudent to examine the raw data very carefully to decide whether data transformation is appropriate.
- The frequency distributions of many water quality and pollution load variables (Chapters 4 through 8) were found to be normally distributed, or at least symmetrically distributed, around a value of central tendency (see for example, Figures 4.5 and 8.1e). Numerous other variables had frequency distributions that exhibited positive skewness.
- An additional univariate statistic, the coefficient of variation (CV) is included in the Tables in Chapters 4 – 8. The coefficient of variation, usually expressed in percent (CV%), is defined as the ratio of the standard deviation to the mean multiplied by 100. This is a useful approximate guide to the degree of variation in a parameter. In general, a $CV < 30\%$ represents a stable, in control variable. In Chapters 4 through 8, most of the parameters showed much larger variation, principally because of the effects of extreme events. Use of the coefficient of variation with log transformed data may result in extreme distortion because the transformation leads to a mean of small value, resulting in a divisor of the ratio that is small and thus a CV that is inflated.
- One additional parameter of interest is the number of days between sampling events. This should be approximately constant, because any outlying results could distort relationships between other parameters.

Bivariate Analysis

Bivariate analysis is used to examine the relationship between pairs of variables.

- The correlation coefficient (r) is usually used to represent the (linear) relationship between any pair of variables. The coefficient of determination (r^2) is, however, a better measure of the intensity of the association between a pair of variables. For example, $r = 0.7$ looks large because the range of r is from -1 to $+1$, but it means that $r^2 = 0.49$ or 49% of the variation is common to the two variables and therefore, 51% of the variation is “unexplained” by the association. It is necessary, therefore, to realize that one needs $r > 0.8$ to claim that a strong association exists; i.e., $> 64\%$ in common.

- Generally, the correlations between concentration parameters were not strong, except for those that are known to be related (e.g., pH and acidity, total and ferrous iron).
- Bivariate analysis of some data sets (e.g., Ernest site data, Chapter 6) showed a strong association between all pairs of the load variables ($r^2 > 80\%$, see Figures 6.5a, b and c). This clearly suggests that because discharge is the common factor in converting concentration to load, it tends to overwhelm the relationships among the other variables.
- Heteroscedasticity occurs when the variation between the parameters increases as their values increase (see Figures 6.5a and 6.5c). In general, to correct for heteroscedasticity, it is advisable to plot the logs of the values to make them homoscedastic and to calculate correlations using log-transformed values.
- Cross-correlation analysis is performed to determine whether there is any lag in correlations between pairs of variables; i.e., to see if a relationship that is weak at zero lag is stronger at greater lags. This observation could result from a delayed effect, where one variable does not associate with another variable immediately, but only after a specific lag or period of time. For example, in a small watershed, where base flow is dominated by several large abandoned deep mine discharges, the peak of concentrations and pollution loads of acidity, iron and other parameters may occur several days or weeks following the peak of streamflow, due to the residence time in the groundwater system.
- The cross-correlation function (CCF) calculates the linear association between observation 0 to t days and so gives a picture of when the association is strongest. In the use of the cross-correlation function in bivariate and time series analyses in this report, r values of 0.2 or the more conservative $r = 0.3$ have been selected as critical values. This selection infers that r values less than these critical values are not significantly different than 0, and therefore can be deleted from consideration. Even if a lag correlation is significantly greater than 0, the relationship may still be weak (low r^2). In most of the examples presented in this report, there did not appear to be any very significant lag in the effects.

Time Series

Two fundamental aspects to the time series analyses (described in Chapters 4 through 8 and Appendix A) are: (1) the use of a simple time series plot of the data for a particular water quality or flow variable, with or without quality control limits, to assist in evaluating patterns of variation through time (essentially an exploratory data analysis step), and (2) the application of the full Box-Jenkins time series analysis and model building procedures (see Figure 9.2).

- Time series analysis begins with a plot of the observations against time (days or dates). This plot is a simple outcome and can give helpful guidance to the type of time series that is represented by the variation in the data. With this graph, outliers plotting beyond the confidence limits are easily seen, and the arrangement of the outliers may be either irregular (occurring as unique individuals) or systematic (e.g., periodic).
- The first step of Box-Jenkins time series analysis is to identify a tentative model and to improve on the model by iteration through the procedure, until a more satisfactory model is found. The basis for identification of a suitable model is the autocorrelation function (Acf) and the partial autocorrelation function (Pacf) of the observations. The form of the Acf and Pacf is usually adequate to determine an appropriate model and one may then proceed to the estimation stage.

- Given the model, it is necessary to estimate the parameters for best fit. Diagnostics are applied to determine if the model is adequate and may also be used to compare different models to select the most appropriate. In order to fit a model with reasonably reliable estimates, there should be at least 2-3 years of data collected at even time intervals (e.g., either weekly or monthly).
- The last step of Box-Jenkins time series analysis is to make predictions or forecasts of future values based on the selected model. This last step was shown to be of little value because extreme events inflated the confidence limits around the forecasts and thus, were not useful.
- There are many alternative extensions of the analytical time series procedure that could have been followed, but because of extreme events, and because of difficulties with missing data and unequal values of t (intervals between collection times), it was considered imprudent, for the purposes of this report, to pursue the analysis further.
- Most of the variables show the presence of a trend over time (pH, flow, acidity, acid load, iron load, ferrous iron). These variables need a first difference to remove the effects of the trend. It seems evident from the studies to date that a moving average model applied to the first differences is almost universally the best choice. In some cases, the autoregressive model, possibly with a first difference, is also appropriate. In both cases, there is an indicator that the variation in whichever parameter is being analyzed, when first differenced, leads to a random walk (the parameter is equally likely to move in one direction as the other, i.e., there is no trend).
- It is somewhat surprising that there appears to be no seasonal component in the time series models, particularly in the load variables. The only satisfactory explanation appears to be the existence of too many maxima at too many different times with very little repetition during the same time period.

Quality Control

There are many methods for defining quality control limits and there are arguments for and against all of them. Throughout this report the conventional quality control limits based upon the mean and standard deviation of the normal frequency distribution are compared to another set of non-parametric quality control limits based upon the median and other order statistics (e.g., quartiles, H-spreads, C-spreads), which may be more applicable to mine drainage data that frequently do not follow a normal distribution.

- The quality control analyses suggest that either the mean (plus or minus two standard deviations) or the non-parametric median (plus or minus a function of the H-spread) are equally appropriate. For the present, it is recommended both should be used until one or the other show superior performance.
- The quality control approach used in this report and much of statistical work in general, is dependent upon the frequency distribution of the sample data. As 95.46% of the area of the normal frequency distribution is contained in the interval of the mean \pm two standard deviations, it is expected that approximately 95 out of 100 observations will occur within these confidence intervals. In the normal frequency distribution, the values are symmetrically distributed around the mean and the mean and standard deviation are best statistical estimators of the population. In a highly skewed frequency distribution, the mean may not be

the best estimator of central tendency, and the standard deviation may not be the best measure of dispersion.

- Quality control limits can be set to compare to a specific number of remaining results by setting a specific value of N' for the equations defined in the chapters. These limits can be used as a subtle trigger for a mean or median, depending on the distribution or data. A quick trigger can also be set in the same manner by setting $N'=1$. For example, if one measurement is to be taken per month for a remaining year, $N'=12$ can be used (equation, page 3-9) to set a subtle trigger for the baseline median.
- The quality control approach should provide adjustments so that the number of monitoring samples (N) and the number of baseline samples (N) can be set to be equal when comparing these time periods (i.e., monitoring $N=12$ should be compared to a baseline $N=12$ even if the baseline contains 36 or more samples from several water years.
- Since intervals based on the median and interquartile range are non-parametric, data does not have to be transformed for normal distribution. However, it is still recommended that the data are graphed, evaluated, and transformed if transformation would improve distribution. This improved distribution would lead to improved statistical control and a tighter estimate of the confidence belts around the median.
- The analyses presented in this report were conducted using long-term data sets with frequent samples. It would be impractical to expect this type of analysis for a remaining operation. Although large data sets are preferable, the practical alternative is to employ a simple quality control approach that allows the use of data sets that are typically compiled for remaining permits.

APPENDIX - A

Hamilton Discharge Data

Appendix A: Hamilton Discharge Data

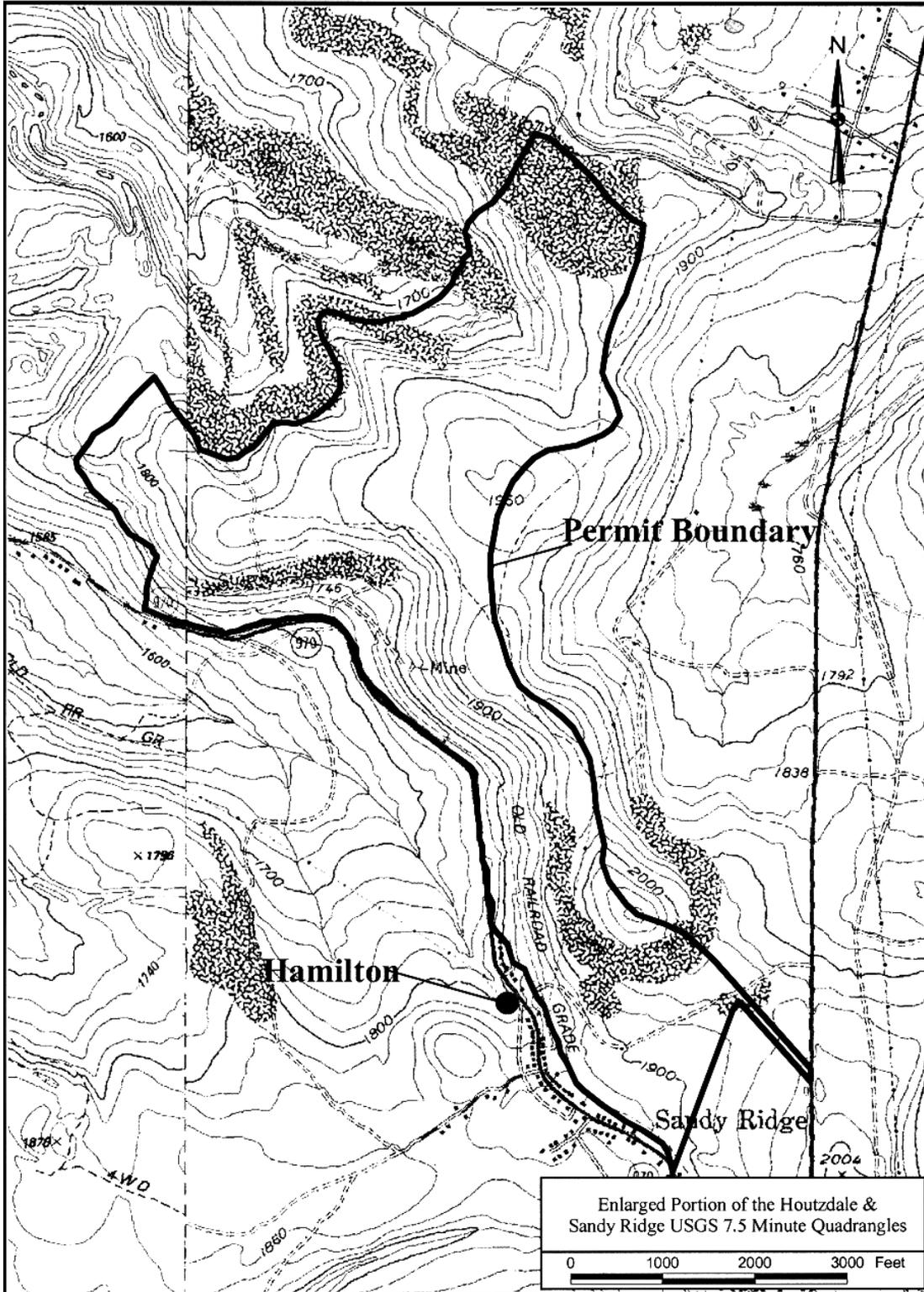
The Hamilton site is a permitted remining site located in Clearfield County, Pennsylvania, as shown in Figure A.1. Several years of background (pre-mining) baseline data existed for two abandoned mine discharges on the site (Hamilton 01 and Hamilton 08). This site was selected to be the initial data set statistically analyzed by Dr. J.C. Griffiths during February to April of 1987. The first two reports of the eight report series of statistical analyses completed by Dr. Griffiths in 1987 and 1988 were on the Hamilton site. Report No. 1 was a preliminary evaluation of the MINITAB¹ software package for the analysis of remining data, performed on the Hamilton 01 and 08 data files. Report No. 2 was an evaluation of the usefulness of MINITAB in conducting a time series analysis, including Box-Jenkins procedures, of the Hamilton 08 discharge data set. Since these first two reports were preliminary or exploratory in nature, they were not as well developed as far as evaluation of the various steps of the data analysis algorithm (see Figure 3.1) as succeeding reports (Report Nos. 3 – 8). These succeeding reports are the subject of Chapters 4 through 8 of this report (Report No. 8 of the original Griffiths report was a synopsis of Report Nos. 1 to 7). However some items of interest, not found in the other reports, were expressed in the Hamilton site reports, and the data set is a good example of remining permit data. Thus, it was determined that the elements of these two reports (although somewhat sketchy in places) and the data sets would be presented in this Appendix.

The Hamilton 01 data had problems (missing data and the presence of a few exceptionally high values) similar to the other data sets described in Chapters 4 through 8. For high values of manganese and sulfate, for example, it was stated that it is important to decide whether to keep or reject the values as outliers with the assumption they are data recording errors and therefore, not really meaningful. Examination of each example, case by case, is recommended to make an appropriate decision. Logarithmic transformation of some variables was attempted, but introduced negative skewness in the sulfate data. Ultimately, it was determined that the sulfate data appeared to be acceptable without transformation.

Some univariate and bivariate analyses were conducted on the Hamilton 08 discharge data. It was found that there was no obvious relationship between flow and acidity. There also was no apparent relationship between acidity and sulfate. There seems to be a weak inverse relationship between manganese and flow (flow increases as manganese decreases). Simple time series plots of acidity, iron, manganese, and sulfate data from the Hamilton 08 discharge were also performed, and some obvious cycles were observed.

¹MINITAB is a commercial software package from Minitab, Inc. ©1986, 3081 Enterprise Drive, State College, PA 16801.

Figure A.1: Map of Hamilton Site



Following application of stem and leaf plots, box plots, scatterplots and time series plots, it was determined that Cross-Correlation functions, Rootogram functions, and the Box-Jenkins procedures in the software package should be applied. It was also concluded that many additional analytical tools could be used including analysis of variance, t-tests, Chi-Square tests, and regression. It is necessary to emphasize that while these tests are easy to apply, both their applicability and the interpretation of the results may be very demanding.

The objective of Griffiths Report No. 2 was an attempt to fit a model to the Hamilton 08 discharge data, and preferably, to find a single simple model that would provide a reasonably close fit. It is desirable to find a single model, if feasible, for all five variables. The Box-Jenkins time series analysis procedure was used for this purpose (Box and Jenkins, 1970). This procedure consists of a convenient package of computer programs that embrace the entire modeling process. A wide variety of models, collectively known as the ARIMA models, is available in this package. Use of this sophisticated procedure requires that the data be collected at equal time intervals. This requirement was only partially fulfilled by the Hamilton 08 data. Therefore, application of the resulting model(s) should be limited.

Eventually, when the model meets the demands of the criteria, it may be used to forecast future values of the variable, accompanied by an appropriate estimate of the confidence limits at a selected probability level. Any new observations may be added to the chosen model and the fit examined for acceptance or rejection. These data should be taken at the same time intervals as the original series (i.e., if the original observations are taken at two week intervals the new observations should also be taken at two week intervals). The number of samples need not be extensive; six to twelve would be acceptable.

If second differences of the flow data set are taken, the Acf and Pacf show many large spikes suggesting that the series has been overdifferenced. It therefore seems evident that an MA (0,1,1) model may be most suitable. The first check criterion is a measure of correlation among the parameters. Since, in this case, there is only one parameter, this does not apply. The second criterion is the Acf of the residuals; if the model "fits" well, all systematic variation has been removed and the remainder is random (equals white noise). There are two tests at this stage: the first is an overall Portmanteau test (Box-Pierce-Ljung Statistic) of all autocorrelations taken together. For this case the result is $X^2 = 17.95$ with 29 degrees of freedom. It is not significantly greater than that expected from white noise, hence it is feasible to consider that these residuals represent random variation and, on the basis of this criterion, there is no evidence to reject the model.

The second test is to examine the individual autocorrelations against twice their standard errors. Since none exceed this value there is no evidence to require further refinement in the model. When first differences of the residuals are taken, the Portmanteau test yields a highly significant value, implying overdifferencing. The Pacf of the residuals confirms this diagnosis.

A number of alternative models were fitted to log-transformed flow data and the results are summarized in Table A.1. Both the AR (1,0,0) and MA (0,1,1) models fit equally well. The coefficient (Φ) in the AR model is approximately equivalent to the first difference in the MA model. Attempts to improve on these simple models by using additional coefficients, seasonal and otherwise, failed to provide any substantial improvement. Thus, it was decided to select one of the simpler models.

Table A.1: Alternate Models Fitted to Log Flow Data

No.	Model	Residual Sum of Squares	Coefficients	Acf spikes	Portmanteau Chi-Square statistic	Residual Standard Deviation
1	MA (0,1,1)	30.73	*	None	17.95	0.519
2	AR (1,0,0)	28.57	*	None	27.58	0.503
3	AR (1,1,1)	30.34	θ_1 not significantly different from 0	None	17.89	0.520
4	AR (2,0,0)	28.57	Φ_1, Φ_2 significantly correlated	None	27.58	0.505
5	AR (1,1,0)	30.83	*	None	19.88	0.522
6	AR (1,0,0) (1,0,0)	25.72	*	None	22.11	0.481
7	AR (1,0,0) (0,0,1)	29.81	Φ_1 not significantly different from 0	None	13.40	0.523

* All coefficients are significantly different from 0 or 1, and there are not significant correlations between coefficients

It was concluded that the most appropriate model, common to all variables, is the simple moving average of the first differences of the observations, or an MA (0,1,1) model. The resulting equations for each variable are:

$$\text{Log Flow} \quad z_t = z_{t-1} + a_t - 0.415a_{t-1}$$

$$\text{Log Acidity} \quad z_t = z_{t-1} + a_t - 0.381a_{t-1}$$

$$\text{Log Fe} \quad z_t = z_{t-1} + a_t - 0.824a_{t-1}$$

$$\text{Log Mn} \quad z_t = z_{t-1} + a_t - 0.662a_{t-1}$$

$$\text{SO}_4 \quad z_t = z_{t-1} + a_t - 0.408a_{t-1}$$

The model implies that the observation at time t (z_t) equals its previous value plus a contribution

from the shock term (a_t) and an additional, smaller contribution from the shock term of the previous period (a_{t-1}). The system appears to have only a one-step memory and is otherwise a typical random variable.

The absence of a seasonal component may be attributed to the fact that there are extreme variations in the data which tend to smother any smaller systematic contribution. There appears to be two main reasons for this, one of which may be modified. The first is the presence of zeros in the data and the absence of an attempt to smooth the data. Smoothing may well be of major importance in reducing the effects of extreme variations and thus, reducing the confidence limits around forecasts. The second reason is that the unusual events represented by large positive residuals are not repeated at the same interval during each annual cycle. Thus, a heavy influx of water from spring melt is common but is not consistently heavy, and rarely occurs on the same date. Again, there are heavy late spring storms which lead to flooding, but do not occur every year and do not always occur in the same month. Thus the spread of events from February to June would tend to smooth out any persistent cyclical feature that may be present. A much longer series would be needed to check these possible effects.

There is one other aspect to the data that may be of importance. It may not be desirable to perform a test of the observations that is too stringent, because it could result in too many false alarms. Thus, a fairly simple, robust test is desirable in practice. The present MA models may well be adequate for this purpose. Investigations at more locations may help to clarify these questions.

Hamilton 01

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
1	0	9.70	337.0	43.30	5.12	868.0
2	34	3.00	360.0	20.00	6.80	900.0
3	73	10.00	305.0	14.00	9.00	652.0
4	119	0.00	400.0	33.00	8.00	823.0
5	161	0.00	294.0	25.00	3.00	422.0
6	202	0.00	307.0	19.00	4.00	550.0
7	216	0.00	305.0	27.00	4.00	342.0
8	231	0.00	300.0	19.00	4.10	419.0
9	244	28.61	539.0	8.50	3.00	142.0
10	257	7.71	195.0	35.00	2.90	430.0
11	271	28.00	174.0	16.20	5.00	494.0
12	286	7.70	184.0	16.00	8.20	510.0
13	299	7.70	230.0	21.50	4.00	600.0
14	313	7.70	306.0	28.00	7.00	612.0
15	329	7.70	254.0	28.00	11.30	382.0
16	342	7.70	394.0	35.00	10.00	423.0
17	356	7.70	444.0	19.00	5.30	705.0
18	369	7.70	340.0	35.00	7.20	399.0
19	383	0.00	474.0	75.00	8.00	872.0
20	386	2.10	714.0	75.00	8.20	608.0
21	411	82.00	222.0	62.00	4.60	550.0
22	425	7.70	258.0	54.30	7.70	500.0
23	455	28.60	274.0	7.00	7.00	550.0
24	467	28.00	282.0	42.00	56.00	700.0
25	482	28.00	284.0	20.00	5.10	510.0
26	495	28.00	268.0	20.00	5.90	681.0
27	510	61.30	220.0	9.50	4.80	620.0
28	524	105.00	202.0	7.20	4.90	598.0
29	538	28.00	214.0	10.00	5.20	613.0
30	552	105.00	110.0	3.70	2.30	587.0
31	565	105.00	118.0	8.00	2.90	358.0
32	579	105.00	162.0	14.70	5.00	469.0
33	593	28.00	224.0	25.00	3.80	655.0
34	608	28.00	250.0	25.00	4.90	713.0
35	624	28.00	98.0	12.50	4.50	477.0
36	636	105.00	197.0	19.00	4.00	397.0
37	650	28.00	78.0	6.00	3.70	612.0
38	666	7.70	264.0	18.00	5.00	600.0
39	680	28.00	218.0	5.20	3.00	542.0
40	692	28.00	286.0	10.00	5.90	643.0
41	706	0.00	458.0	13.00	6.50	746.0
42	721	7.70	352.0	8.50	7.50	811.0
43	734	0.00	356.0	6.90	7.30	778.0
44	748	2.10	632.0	9.30	7.90	568.0
45	762	7.70	392.0	8.70	9.30	831.0
46	772	2.10	364.0	9.00	8.00	806.0
47	790	7.70	336.0	7.50	8.00	835.0

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
48	799	7.70	334.0	7.00	8.00	798.0
49	818	7.70	316.0	9.00	7.00	655.0
50	832	7.70	306.0	9.00	6.00	713.0
51	846	7.70	370.0	12.80	4.90	794.0
52	857	7.70	306.0	9.00	8.00	674.0
53	867	7.70	346.0	9.00	8.00	719.0
54	874	28.00	206.0	8.00	5.53	431.0
55	885	28.00	264.0	8.00	6.00	566.0
56	899	28.00	264.0	10.00	6.00	594.0
57	916	105.00	261.0	3.75	4.00	333.0
58	930	61.00	226.8	2.25	3.00	29.6
59	944	61.00	155.6	4.00	3.00	276.0
60	958	61.00	133.4	2.75	2.30	181.0
61	972	61.00	168.1	4.20	3.90	300.0
62	989	29.00	74.2	9.80	5.10	343.0
63	1000	28.97	142.2	8.00	7.80	491.0
64	1015	7.80	158.3	12.00	6.00	550.0
65	1028	0.00	191.3	7.50	9.00	511.0
66	1043	7.80	232.6	9.00	10.00	584.0
67	1052	7.80	266.8	7.50	7.00	690.0
68	1070	7.80	300.7	9.50	19.00	531.0
69	1085	7.80	317.3	8.00	14.00	452.0
70	1098	7.80	326.6	9.50	11.50	755.0
71	1116	1.20	314.7	6.00	10.00	805.0
72	1126	2.20	287.3	8.50	9.00	816.0
73	1141	7.90	265.6	7.50	9.00	780.0
74	1154	6.10	184.5	8.00	9.50	608.0
75	1171	8.90	121.2	9.00	4.40	300.0
76	1184	41.70	91.6	3.10	3.30	261.0
77	1197	2.20	166.1	5.50	4.80	396.0
78	1210	197.00	197.0	8.50	5.30	524.0
79	1221	0.00	226.1	6.50	7.30	652.0
80	1238	61.00	215.7	8.00	7.50	609.0
81	1248	131.00	84.6	1.20	2.90	187.0
82	1266	0.00	107.8	4.00	2.20	242.0
83	1280	7.90	126.7	6.50	3.50	337.0
84	1294	18.80	107.1	3.90	2.80	246.0
85	1308	12.10	128.2	6.00	2.80	264.0
86	1322	11.00	126.7	7.30	3.60	284.0
87	1336	8.90	124.7	6.30	2.90	255.0
88	1351	12.00	102.4	5.50	2.40	236.0
89	1365	2.70	190.4	9.00	6.30	455.0
90	1379	4.60	179.4	6.50	5.50	385.0
91	1393	4.60	189.3	7.00	4.30	481.0
92	1407	2.70	202.3	8.00	7.80	596.0
93	1421	4.60	664.7	8.00	6.50	466.0
94	1434	12.10	163.8	3.90	3.20	299.0
95	1450	4.60	194.3	3.90	4.60	466.0
96	1464	9.90	231.5	8.50	5.50	612.0

Appendix A

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
97	1477	5.40	265.6	9.50	9.80	700.0
98	1487	2.70	264.7	8.50	9.80	1223.0
99	1504	4.60	447.7	1.60	10.60	716.0
100	1515	4.60	287.2	1.82	10.30	667.0
101	1526	2.20	282.8	11.82	7.50	664.0
102	1548	27.10	175.1	4.76	10.71	369.0
103	1581	23.60	201.8	4.57	6.07	362.0
104	1599	14.60	238.3	3.94	2.40	613.0
105	1623	54.30	120.5	1.77	1.66	275.0
106	1688	18.80	200.8	6.90	4.50	395.0
107	1700	18.80	198.1	5.99	4.61	326.0
108	1711	15.90	218.0	5.90	5.44	504.0
109	1731	8.90	250.0	44.80	11.30	603.0
110	1742	13.30	222.0	6.22	21.50	509.0
111	1760	15.90	259.0	3.70	10.70	621.0
112	1770	9.90	324.0	3.62	6.48	617.0
113	1784	7.90	305.0	3.76	6.51	622.0
114	1798	7.90	492.0	6.51	6.52	641.0
115	1814	8.90	625.0	9.06	5.83	609.0
116	1826	9.90	294.0	8.83	7.07	721.0
117	1842	11.00	356.0	10.40	7.59	802.0
118	1855	3.30	359.0	6.28	6.74	840.0
119	1865	4.00	355.0	10.60	7.52	874.0

Hamilton 8

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
1	0	0	298	16.1	4.49	750
2	132	0	291	15	4.5	202
3	155	0	291	19	6	141
4	170	0	221	21.1	6	170
5	202	0	250	15	4.5	184
6	244	70	300	28	6	166
7	258	33	226	11	5.1	183
8	272	33	272	19	3.2	145
9	287	33	236	27	9.5	199
10	300	33	262	30	9	200
11	314	33	348	23	8	240
12	330	19	376	25	5	160
13	343	9	404	120	4.3	184
14	357	9	490	25	9	300
15	370	9	416	38	2	161
16	384	9	558	40	4.9	848
17	398	9	448	40	6.8	300
18	412	2	344	21.5	7	750
19	426	9	362	40	7.5	262
20	456	9	328	13	8.1	675
21	468	9	356	33.7	6.5	650
22	483	19	290	29	5.4	700
23	496	32	238	10.5	5.5	677
24	511	32	270	13.7	5.6	693
25	525	32	254	17.2	5.5	647
26	539	19	256	17	6.5	649
27	553	120	204	14	3.8	662
28	566	70	216	13.7	4.5	487
29	580	32	224	12.9	10	495
30	594	19	238	14.7	3.4	591
31	609	32	278	14.7	5	680
32	624	32	232	18.68	4.6	600
33	636	32	219	5.99	5.1	493
34	650	32	187	4.8	3.9	575
35	666	9	386	16	5	498
36	680	32	336	7.11	3.5	702
37	692	32	320	16.1	8.5	707
38	706	0	660	7.5	6.5	751
39	721	9	382	8.5	8	801.99
40	734	0	340	8.5	5.5	797
41	748	2	454	7.5	8.2	592.99
42	762	9	460	11.5	10.1	862.01
43	772	2	414	7.5	7	851
44	790	9	390	10	10	993
45	799	9	394	7.5	10	894.99
46	818	9	396	11	6	752
47	832	9	370	7.5	5	852

Appendix A

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
48	846	9	430	9.8	6.2	774
49	857	9	472	9	9	819.99
50	867	9	448	8	7	817
51	874	32	270	10	6	514
52	885	9	292	8	6	543
53	899	9	372	9	8	629
54	916	49	409.4	11	5.5	449
55	930	120	324.2	8.5	3.5	365
56	944	70	282.2	6	4	363
57	958	70	283.8	10	3.8	275
58	972	32	270	4.8	2.2	322
59	989	19	112.6	11.5	6.2	390
60	1000	19	164.8	7.9	6.9	453.99
61	1015	8.9	178.4	11	7	517
62	1028	8.9	204.2	8	7	516
63	1043	8.9	247.7	10	6.3	588.99
64	1052	8.9	178.4	8.5	1.3	180
65	1070	2.4	320	8.5	12	396
66	1085	8.1	339	11	10	466
67	1098	6.7	342.1	17	9.5	791.01
68	1116	1.8	376.8	7.5	10	879
69	1126	3.3	340.9	9.5	10.5	808
70	1141	6.1	338.1	8	11	910
71	1154	5.4	291	14	13	854
72	1171	18.8	252.1	8	10	510
73	1184	72.3	151.5	7	5.3	382
74	1197	44	238.7	6	5.3	465
75	1214	18.8	254.4	8	6.5	555
76	1221	18.8	283	8	8	676.01
77	1238	9.9	309.4	8.5	10	677
78	1248	360	141.9	5.5	3.4	294
79	1266	37.1	197.9	7	4.5	436
80	1280	12.1	206.6	8.5	5	464
81	1294	46.7	198.3	9	4	334
82	1308	62.8	214.8	8.5	3.2	313
83	1322	44	202.8	8	4.3	335
84	1336	37	212	7	3.4	343
85	1351	49	189	7	4.3	345
86	1365	22	223.1	12	5.3	440
87	1379	17	232.9	7.5	5.3	413
88	1392	12	270.8	7	4.8	543
89	1407	7.9	270.8	8.3	8	621
90	1421	14.6	310.8	8.3	8.5	669.99
91	1434	25.3	221.2	8	4.5	443
92	1450	12.1	273.6	8.4	4.6	552
93	1464	11	294.1	8	6.8	618
94	1477	8.9	329	9	10	625
95	1487	7.9	232.6	7.5	11	667.01
96	1504	6.2	369.6	3.1	12.1	911

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

Rows	Days	Flow	Acidity	Total Iron	Manganese	Sulfate
97	1515	7.1	375.1	3.3	12.6	746
98	1526	7.1	371.6	11.6	9	827.01
99	1548	23.6	292.5	16.46	13.83	494.99
100	1581	37.1	238.2	9.15	6.02	600
101	1599	25.3	271.2	8.5	2.31	561
102	1623	140	171.2	4.56	2.18	311
103	1688	57	225.7	13.8	4.55	481.01
104	1700	44	228.3	12.22	4.7	299
105	1711	32.9	259	8.9	5.42	527
106	1731	23.6	298	0.1	8.43	616
107	1742	21.9	294	13.4	14.1	569
108	1760	21.9	329	19.7	5.51	646.99
109	1770	17.3	360	17	7.37	629
110	1784	15.9	347	16.5	7.44	634
111	1798	14.6	381	14.4	6.57	640
112	1814	14.6	394	17.1	5.6	801
113	1876	13.3	401	17.3	5.58	846.99
114	1842	12.1	401	15	7.96	858.01
115	1855	11	408	13.3	6.72	879
116	1865	8.9	451	16.2	7.82	874

APPENDIX - B

Arnot Discharge Data

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

Arnot 001

ROW	DATE	PH	TEMP	ACIDITY	ALK	TOT. FE	FFE	SO4	CA	MG	MN	AL	DISCH	flow gpm	DATE
1	1/28/80	5.02	ND	12	4	0.2	0.1	180	ND	ND	ND	ND	0.531	238.33	29248
2	2/29/80	4.86	9.8	23	4	0.2	0.2	96	ND	ND	ND	ND	0.291	130.61	29280
3	3/31/80	5.08	7.6	9	4	0.3	0.2	91	ND	ND	ND	ND	2.375	1065.97	29311
4	4/22/80	5.03	8.4	14	8	0.4	0.3	122	ND	ND	ND	ND	1.474	661.58	29333
5	5/10/80	4.83	9.2	13	7	0.3	0.2	141	93	77	1.58	0.63	1.240	556.55	29351
6	5/31/80	4.82	10.8	12	8	0.2	0.0	177	96	67	1.62	0.70	0.514	230.70	29372
7	6/18/80	4.70	11.0	27	3	0.2	0.1	181	118	64	1.69	3.64	0.446	200.18	29390
8	6/30/80	4.68	11.3	23	2	0.3	0.3	186	107	82	1.68	0.73	0.366	164.27	29402
9	7/19/80	4.50	9.9	28	0	0.2	0.1	177	111	82	1.34	0.81	0.466	209.15	29421
10	8/12/80	4.73	11.2	31	7	0.2	0.1	204	121	80	1.85	1.57	0.241	108.17	29445
11	8/27/80	4.68	12.9	24	6	0.3	0.2	206	115	90	1.86	1.39	0.241	108.17	29460
12	9/11/80	4.89	9.8	31	6	0.3	0.2	182	133	95	1.78	2.67	0.196	87.97	29475
13	9/27/80	4.91	8.9	28	6	0.2	0.2	193	135	99	1.92	2.71	0.150	67.32	29491
14	10/16/80	4.66	9.3	35	5	0.3	0.2	240	136	124	1.71	2.87	0.209	93.81	29510
15	11/7/80	4.97	9.6	41	37	0.1	0.1	211	130	113	2.44	1.93	0.209	93.81	29532
16	11/30/80	4.20	8.6	28	0	0.1	0.1	259	144	114	1.87	2.23	0.209	93.81	29555
17	12/18/80	4.75	7.6	28	5	0.3	0.3	231	152	103	2.52	3.19	0.209	93.81	29573
18	1/5/81	4.92	9.1	26	18	0.2	0.1	179	146	145	2.67	2.29	0.209	93.81	29591
19	1/19/81	4.77	7.5	27	9	0.3	0.1	228	139	141	2.70	2.60	0.178	79.89	29605
20	1/31/81	4.92	9.1	26	18	0.2	0.1	179	141	127	2.68	2.87	0.193	86.62	29617
21	2/19/81	5.02	7.0	8	7	0.3	0.2	117	70	67	0.82	0.19	0.010	4.49	29636
22	3/8/81	5.07	8.0	16	7	0.1	0.1	159	80	76	1.61	0.92	1.332	597.84	29653
23	3/21/81	5.03	8.0	15	6	0.1	0.1	151	83	87	1.41	0.91	0.718	322.26	29666
24	4/11/81	5.02	8.7	6	18	0.2	0.0	140	91	76	1.50	0.36	0.718	322.26	29687
25	4/30/81	5.38	8.3	12	12	0.2	0.2	131	79	69	1.28	0.22	1.063	477.11	29706
26	5/16/81	5.45	8.3	10	16	0.2	0.0	134	76	76	1.04	0.27	1.332	597.84	29722
27	5/29/81	5.03	9.0	11	5	0.3	0.1	124	96	68	1.41	0.50	0.862	386.89	29735
28	6/18/81	5.13	12.0	10	5	0.2	0.1	154	120	80	1.79	0.97	0.542	243.27	29755
29	6/30/81	5.10	8.9	9	11	0.2	0.0	151	90	86	1.24	ND	0.673	302.06	29767
30	7/13/81	4.95	9.4	16	7	0.2	0.2	140	99	90	1.55	0.35	0.584	262.12	29780
31	7/28/81	4.72	8.6	19	6	0.2	0.2	188	129	81	2.33	0.94	0.420	188.51	29795
32	8/30/81	4.84	11.3	28	4	0.2	0.0	195	120	105	2.49	2.04	0.274	122.98	29828
33	9/29/81	4.63	9.1	31	7	0.2	0.1	210	130	118	3.95	2.28	0.209	93.81	29858
34	10/15/81	4.50	9.8	33	0	0.2	0.2	244	129	125	3.80	2.52	0.209	93.81	29874
35	10/29/81	4.69	9.1	39	6	0.2	0.1	205	124	111	2.75	2.08	0.241	108.17	29888
36	12/8/81	4.82	7.9	12	5	0.2	0.2	186	102	92	2.17	1.51	0.459	206.01	29928
37	12/16/81	4.84	8.3	15	14	0.2	0.2	189	108	83	1.77	1.12	0.420	188.51	29936
38	1/6/82	5.04	7.8	13	8	0.2	0.0	185	111	75	1.87	1.70	0.500	224.42	29957
39	1/14/82	5.02	ND	12	8	0.2	0.1	106	79	46	1.02	0.68	0.673	302.06	29965

Appendix B

ROW	DATE	PH	TEMP	ACIDITY	ALK	TOT. FE	FFE	SO4	CA	MG	MN	AL	DISCH	flow gpm	DATE
40	2/23/82	5.22	7.3	16	5	0.3	0.2	160	ND	ND	ND	ND	0.861	386.44	30005
41	3/2/82	5.01	8.4	10	4	0.2	0.1	172	115	58	1.16	0.10	0.673	302.06	30012
42	3/31/82	5.05	8.9	8	7	0.2	0.0	107	80	58	0.98	0.25	2.912	1306.99	30041
43	5/6/82	5.13	9.0	13	14	0.3	0.2	124	110	54	0.95	0.50	0.910	408.44	30077
44	5/19/82	4.96	ND	19	7	0.2	0.2	148	99	101	ND	ND	0.584	262.12	30090
45	5/26/82	4.78	ND	12	9	0.2	0.0	118	100	83	0.74	0.87	0.628	281.87	30097
46	6/2/82	4.92	ND	64	11	0.2	0.0	151	95	82	0.68	0.58	0.765	343.35	30104
47	6/10/82	5.34	ND	10	16	0.4	0.2	99	66	51	0.85	0.51	3.484	1563.72	30112
48	6/11/82	5.10	9.2	8	11	0.3	0.2	130	68	77	0.95	0.27	3.124	1402.14	30113
49	6/16/82	4.94	9.0	10	9	0.3	0.1	170	118	46	1.11	0.45	1.984	890.48	30118
50	6/25/82	4.92	10.0	14	9	0.2	0.1	186	125	42	1.22	0.56	1.168	524.23	30127
51	6/30/82	5.19	ND	13	8	0.2	0.1	185	93	71	1.39	0.70	0.910	408.44	30132
52	7/1/82	4.91	9.8	11	4	0.2	0.2	148	96	74	1.31	0.61	0.861	386.44	30133
53	7/8/82	4.84	9.8	11	3	0.2	0.2	141	103	72	1.38	0.79	0.178	79.89	30140
54	7/16/82	4.67	10.9	15	13	0.0	0.0	161	102	76	1.60	0.78	0.565	253.59	30148
55	7/28/82	4.78	ND	17	4	0.2	0.1	169	102	87	1.57	1.58	0.437	196.14	30160
56	8/6/82	4.72	ND	15	4	0.2	0.1	171	101	92	1.70	2.00	0.378	169.66	30169
57	8/12/82	4.74	10.5	41	3	0.2	0.2	202	ND	ND	1.68	2.27	0.355	159.33	30175
58	8/17/82	4.69	ND	22	2	0.1	0.0	211	114	93	2.01	ND	0.325	145.87	30180
59	8/26/82	4.67	12.2	25	2	0.0	0.0	198	124	109	0.54	2.96	0.289	129.71	30189
60	9/12/82	4.65	12.5	25	2	0.1	0.1	201	123	104	1.18	2.55	0.246	110.41	30206
61	10/2/82	4.54	11.7	26	2	0.2	0.1	252	130	130	2.24	2.73	0.219	98.29	30226
62	10/16/82	4.48	9.6	40	1	0.2	0.1	238	130	107	2.17	2.64	0.187	83.93	30240
63	10/30/82	4.57	11.7	40	1	0.1	0.1	212	142	107	2.75	3.08	0.210	94.25	30254
64	11/5/82	4.42	ND	31	0	0.1	0.1	252	143	95	2.70	ND	0.199	89.32	30260
65	11/24/82	4.58	7.8	39	2	0.2	0.0	240	137	130	2.66	3.22	0.166	74.51	30279
66	12/16/82	4.59	9.2	37	2	0.2	0.2	277	127	118	2.09	2.98	0.188	84.38	30301
67	1/8/83	4.57	7.8	31	0	0.2	0.0	254	127	128	2.39	3.22	0.216	96.95	30324
68	2/5/83	4.84	7.8	10	4	0.2	0.1	159	150	31	1.45	0.44	0.565	253.59	30352
69	3/1/83	4.94	ND	22	5	0.1	0.0	191	104	116	1.49	1.46	0.569	255.38	30376
70	4/6/83	5.06	8.3	3	6	0.2	0.1	182	82	62	1.29	0.80	1.613	723.96	30412
71	4/23/83	4.97	9.0	6	4	0.2	0.1	125	70	69	1.40	0.60	2.617	1174.59	30429
72	5/5/83	4.86	8.6	9	3	0.2	0.1	171	66	41	0.96	0.51	5.091	2284.99	30441
73	5/10/83	4.99	ND	16	5	0.3	0.1	66	80	77	0.67	1.16	3.032	1360.85	30446
74	5/20/83	4.92	9.2	4	6	0.2	0.1	92	75	70	1.41	1.15	2.112	947.93	30456
75	5/31/83	4.92	8.9	7	6	0.1	0.0	140	81	61	1.32	0.66	1.382	620.28	30467
76	6/14/83	4.81	9.3	8	5	0.2	0.1	132	98	62	1.76	0.69	0.821	368.49	30481
77	6/30/83	4.76	9.7	15	4	0.3	0.1	169	125	54	1.05	0.41	0.673	302.06	30497
78	7/16/83	4.67	11.8	31	3	0.2	0.1	180	118	93	1.92	0.92	0.568	254.94	30513
79	8/2/83	4.64	11.7	23	3	0.2	0.1	189	123	79	1.90	1.60	0.448	201.08	30530
80	8/5/83	4.65	ND	20	2	0.3	0.1	167	123	87	1.92	1.68	0.425	190.75	30533

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	PH	TEMP	ACIDITY	ALK	TOT. FE	FFE	SO4	CA	MG	MN	AL	DISCH	flow gpm	DATE
81	8/14/83	4.68	12.2	25	3	0.4	0.2	220	116	91	2.03	1.94	0.364	163.37	30542
	MAX	5.45	12.90	64.00	37.00	0.40	0.30	277.00	152.00	145.00	3.95	3.64	5.09		
	MIN	4.20	7.00	3.00	0.00	0.00	0.00	66.00	66.00	31.00	0.54	0.10	0.01		
	AVG	4.85	9.45	20.04	6.46	0.21	0.12	173.23	109.52	86.05	1.71	1.43	0.80		
	MED	4.85	9.45	20.04	6.46	0.21	0.12	173.23	109.52	82.00	1.71	1.43	0.80		

Appendix B

Arnot 003

ROW	DATE	PH	TEMP	DISCH	ACIDITY	ACIDL	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
1	1/28/80	3.35	m.v.	0.190	69	32.04	0	0	1.2	0.56	0.5	0.23	162	75.23	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.
2	2/29/80	3.31	8.5	0.117	119	34.14	0	0	1.2	0.34	0.4	0.12	180	51.64	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.
3	3/31/80	3.50	m.v.	0.494	47	56.80	0	0	1.1	1.33	0.3	0.36	93	112.39	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.
4	4/22/80	3.42	8.4	0.360	58	51.05	0	0	1.2	1.06	0.2	0.18	119	104.74	m.v.	m.v.	m.v.	m.v.	1.85	1.63	3.31	2.91
5	5/10/80	3.24	8.5	0.360	70	61.61	0	0	1.0	0.88	0.3	0.26	149	131.14	58	51.05	45	39.61	1.92	1.69	3.76	3.31
6	5/31/80	3.21	8.5	0.360	70	61.61	0	0	0.8	0.70	0.0	0.00	148	130.26	55	48.41	51	44.89	2.40	2.11	3.45	3.04
7	6/18/80	3.29	8.7	0.219	90	48.16	0	0	0.8	0.43	0.3	0.16	169	90.43	61	32.64	66	35.32	2.73	1.46	5.16	2.76
8	6/30/80	3.29	8.9	0.139	81	27.58	0	0	0.8	0.27	0.3	0.10	177	60.26	61	20.77	56	19.07	2.87	0.98	0.88	0.30
9	7/19/80	3.21	8.9	0.128	107	33.61	0	0	0.7	0.22	0.2	0.06	181	56.85	59	18.53	67	21.04	2.48	0.78	4.36	1.40
10	8/12/80	3.26	8.9	0.117	106	30.41	0	0	0.9	0.26	0.6	0.17	208	59.68	66	18.94	70	20.08	4.70	1.35	6.12	1.76
11	8/27/80	3.26	9.0	0.106	99	25.67	0	0	1.0	0.26	0.7	0.18	197	53.93	69	17.89	68	17.63	4.55	1.18	3.85	1.00
12	9/11/80	3.37	8.4	0.092	89	20.13	0	0	1.0	0.23	0.4	0.09	208	47.05	71	16.06	78	17.64	3.70	0.84	5.80	1.31
13	9/27/80	3.37	8.5	0.087	104	22.08	0	0	1.0	0.21	0.4	0.09	191	40.56	74	15.71	72	15.29	4.20	0.89	6.64	1.41
14	10/16/80	3.23	8.9	0.080	102	19.97	0	0	1.0	0.20	0.2	0.04	214	41.89	69	13.51	89	17.42	4.40	0.86	7.09	1.39
15	11/7/80	3.41	8.9	0.072	97	17.16	0	0	0.9	0.16	0.4	0.07	225	39.80	74	13.09	99	17.51	4.90	0.87	7.39	1.31
16	11/30/80	3.31	7.8	0.065	109	17.35	0	0	0.9	0.14	0.1	0.02	218	34.70	77	12.26	95	15.12	4.65	0.74	6.60	1.05
17	12/8/80	3.24	6.9	0.065	108	17.19	0	0	1.2	0.19	0.5	0.08	232	36.93	90	14.33	96	15.28	5.90	0.94	9.40	1.50
18	1/5/81	3.36	6.9	0.052	113	14.36	0	0	1.1	0.14	0.3	0.04	231	29.35	77	9.78	142	18.04	5.70	0.72	9.44	1.20
19	1/19/81	3.17	7.3	0.046	106	11.93	0	0	1.2	0.14	0.3	0.03	215	24.20	77	8.67	127	14.30	6.70	0.75	8.37	0.94
20	1/31/81	3.32	7.3	0.046	104	11.71	0	0	1.2	0.14	0.3	0.03	215	24.20	78	8.78	115	12.94	6.90	0.78	8.03	0.90
21	2/19/81	3.70	6.2	0.363	42	37.30	0	0	0.5	0.44	0.2	0.18	110	97.69	44	39.08	39	34.64	1.95	1.73	0.70	0.62
22	3/8/81	3.36	7.8	0.425	66	68.56	0	0	1.5	1.56	0.1	0.10	158	164.12	46	47.78	49	50.90	2.72	2.82	3.77	3.92
23	3/21/81	3.29	8.1	0.249	83	50.52	0	0	1.5	0.91	0.2	0.12	85	51.74	46	28.00	59	35.91	1.99	1.21	1.79	1.09
24	4/11/81	3.21	8.7	0.226	71	39.26	0	0	1.2	0.66	0.6	0.33	125	69.12	70	38.71	53	29.31	2.62	1.45	1.76	0.97
25	4/30/81	3.46	8.3	0.325	101	80.34	0	0	1.3	1.03	0.3	0.24	150	119.31	52	41.36	64	50.91	3.18	2.53	4.35	3.46
26	5/16/81	3.49	8.3	0.446	140	152.90	0	0	1.2	1.31	0.2	0.22	144	157.27	48	52.42	57	62.25	2.35	2.57	3.23	3.53
27	5/29/81	3.32	8.6	0.325	70	55.68	0	0	1.4	1.11	0.2	0.16	144	114.54	49	38.98	67	53.29	2.07	1.65	3.89	3.09
28	6/18/81	3.41	8.9	0.198	71	34.33	0	0	1.2	0.58	0.2	0.10	165	79.79	56	27.08	66	31.92	2.76	1.34	4.87	2.36
29	6/30/81	3.32	8.7	0.198	79	38.20	0	0	1.1	0.53	0.2	0.10	170	82.21	55	26.60	72	34.82	2.38	1.15	m.v.	m.v.
30	7/13/81	3.27	8.2	0.172	80	33.57	0	0	1.2	0.50	0.7	0.29	171	71.76	54	22.26	74	31.06	2.52	1.06	3.81	1.60
31	7/30/81	3.29	8.6	0.136	87	29.03	0	0	1.1	0.37	0.2	0.07	165	55.06	64	21.36	75	25.03	4.65	1.55	4.80	1.60
32	8/30/81	3.32	9.2	0.106	96	24.89	0	0	1.1	0.29	0.4	0.10	143	37.08	62	16.08	83	21.52	4.80	1.25	6.96	1.81
33	9/29/81	3.13	8.4	0.072	95	16.81	0	0	1.2	0.21	1.0	0.18	211	37.33	60	10.62	103	18.22	6.20	1.10	6.96	1.23
34	10/15/81	3.07	8.9	0.065	114	18.15	0	0	1.3	0.21	0.7	0.11	223	35.50	70	11.14	94	14.96	5.95	0.95	6.52	1.04
35	10/29/81	3.24	8.3	0.066	151	24.50	0	0	1.2	0.19	0.8	0.13	221	35.82	70	11.34	99	16.04	4.60	0.75	5.16	0.84
36	11/23/81	3.22	7.7	0.106	101	26.19	0	0	1.5	0.39	0.5	0.13	231	59.90	64	16.59	99	25.67	4.56	1.18	7.34	1.90
37	12/8/81	3.04	7.8	0.106	111	28.78	0	0	1.6	0.42	0.4	0.10	225	58.34	66	17.11	97	25.41	5.60	1.45	7.09	1.84
38	12/16/81	3.11	7.7	0.106	107	27.74	0	0	1.8	0.47	1.5	0.39	223	57.82	62	16.08	99	25.67	4.50	1.17	6.64	1.72
39	1/6/82	3.27	7.9	0.159	120	46.77	0	0	1.6	0.62	0.3	0.12	212	82.62	61	23.77	81	31.57	4.75	1.85	6.57	2.56
40	1/14/82	3.59	m.v.	0.184	64	28.86	0	0	0.8	0.36	0.4	0.18	122	55.01	61	27.51	40	18.04	1.98	0.89	3.05	1.38

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	PH	TEMP	DISCH	ACIDITY	ACIDLD	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
41	2/23/82	3.21	6.5	0.257	133	83.52	0	0	1.7	1.07	0.5	0.31	167	104.87	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.	m.v.
42	3/2/82	3.15	7.8	0.226	94	51.98	0	0	1.4	0.77	0.5	0.28	179	98.98	58	32.07	82	45.34	2.57	1.42	3.40	1.88
43	3/31/82	3.36	8.5	0.565	57	78.85	0	0	1.0	1.38	0.3	0.42	128	177.07	53	73.32	39	53.95	1.61	2.23	1.90	2.63
44	5/6/82	3.38	8.5	0.363	68	60.39	0	0	1.2	1.07	0.6	0.53	125	111.01	48	42.63	65	57.73	1.88	1.67	1.28	1.14
45	5/19/82	3.28	m.v.	0.338	65	53.77	0	0	1.0	0.83	0.6	0.50	98	81.06	51	42.19	67	55.42	m.v.	m.v.	m.v.	m.v.
46	5/26/82	3.34	m.v.	0.319	60	46.83	0	0	0.9	0.70	0.4	0.31	134	104.59	48	37.47	55	42.93	1.91	1.49	3.40	2.65
47	6/2/82	3.30	m.v.	0.290	58	41.11	0	0	1.0	0.71	0.2	0.14	134	94.97	52	36.85	52	36.85	2.01	1.43	1.75	1.24
48	6/10/82	3.47	m.v.	0.565	50	69.17	0	0	0.8	1.11	0.4	0.55	119	164.62	44	60.87	74	102.37	1.57	2.17	2.90	4.01
49	6/11/82	3.42	9.0	0.516	57	71.93	0	0	1.2	1.51	0.4	0.51	134	169.10	44	55.52	53	66.88	1.61	2.03	2.98	3.76
50	6/16/82	3.31	9.0	0.516	59	74.45	0	0	1.1	1.39	0.2	0.25	128	161.53	48	60.57	69	87.07	1.62	2.04	2.94	3.71
51	6/25/82	3.27	9.0	0.383	59	55.27	0	0	1.1	1.03	0.3	0.28	144	134.89	47	44.03	72	67.45	1.67	1.56	3.26	3.05
52	6/30/82	3.29	m.v.	0.325	60	47.72	0	0	0.9	0.72	0.2	0.16	128	101.81	47	37.38	49	38.97	1.76	1.40	3.56	2.83
53	7/1/82	3.33	9.5	0.307	64	48.09	0	0	1.2	0.90	0.3	0.23	116	87.15	46	34.56	55	41.32	2.01	1.51	3.59	2.70
54	7/8/82	3.35	9.0	0.243	64	38.05	0	0	1.1	0.65	0.2	0.12	146	86.80	45	26.75	49	29.13	1.84	1.09	4.06	2.41
55	7/16/82	3.36	9.7	0.193	79	37.30	0	0	0.7	0.33	0.1	0.05	151	71.30	m.v.	m.v.	m.v.	m.v.	2.30	1.09	m.v.	m.v.
56	7/28/82	3.26	m.v.	0.157	67	25.74	0	0	0.9	0.35	0.3	0.12	137	52.62	53	20.36	55	21.13	2.45	0.94	4.29	1.65
57	8/6/82	3.25	m.v.	0.136	69	22.96	0	0	1.0	0.33	0.3	0.10	165	54.90	58	19.30	72	23.96	2.68	0.89	4.67	1.55
58	8/12/82	3.16	9.0	0.125	97	29.66	0	0	0.9	0.28	0.1	0.03	178	54.44	m.v.	m.v.	m.v.	m.v.	2.83	0.87	4.68	1.43
59	8/17/82	3.24	m.v.	0.115	74	20.82	0	0	0.8	0.23	0.0	0.00	184	51.77	59	16.60	83	23.35	2.80	0.79	m.v.	m.v.
60	8/26/82	3.20	10.3	0.106	80	20.75	0	0	0.8	0.21	0.4	0.10	158	40.98	63	16.34	84	21.78	3.27	0.85	5.43	1.41
61	9/12/82	3.19	10.0	0.089	86	18.73	0	0	0.7	0.15	0.7	0.15	158	34.40	61	13.28	71	15.46	3.61	0.79	6.26	1.36
62	10/2/82	3.21	9.6	0.073	102	18.22	0	0	0.9	0.16	0.2	0.04	220	39.29	67	11.97	67	11.97	3.45	0.62	6.98	1.25
63	10/16/82	3.14	8.6	0.068	104	17.30	0	0	1.0	0.17	0.2	0.03	215	35.77	74	12.31	77	12.81	3.61	0.60	6.96	1.16
64	10/30/82	3.20	10.0	0.065	110	17.49	0	0	0.5	0.08	0.1	0.02	206	32.76	74	11.77	103	16.38	3.79	0.60	7.94	1.26
65	11/5/82	3.18	m.v.	0.058	104	14.76	0	0	0.3	0.04	0.1	0.01	233	33.06	84	11.92	116	16.46	4.04	0.57	m.v.	m.v.
66	11/24/82	3.18	7.4	0.046	114	12.83	0	0	1.0	0.11	0.1	0.01	250	28.14	74	8.33	114	12.83	4.55	0.51	8.29	0.93
67	12/16/82	3.24	8.6	0.040	120	11.74	0	0	1.1	0.11	0.3	0.03	256	25.05	72	7.05	103	10.08	4.68	0.46	9.05	0.89
68	1/8/83	3.15	7.8	0.052	114	14.50	0	0	0.8	0.10	0.2	0.03	262	33.33	80	10.18	102	12.98	4.30	0.55	9.40	1.20
69	2/5/83	3.27	6.8	0.198	81	39.24	0	0	1.1	0.53	0.3	0.15	103	49.90	63	30.52	64	31.00	3.09	1.50	7.88	3.82
70	3/1/83	3.18	m.v.	0.125	103	31.50	0	0	1.5	0.46	0.3	0.09	220	67.28	71	21.71	122	37.31	3.40	1.04	6.78	2.07
71	4/6/83	3.25	8.3	0.361	72	63.59	0	0	2.0	1.77	0.7	0.62	165	145.73	50	44.16	58	51.23	1.54	1.36	3.89	3.44
72	4/23/83	3.25	8.9	0.493	69	83.23	0	0	1.5	1.81	0.4	0.48	145	174.89	45	54.28	48	57.90	1.84	2.22	3.22	3.88
73	5/5/83	3.24	8.5	0.538	86	113.20	0	0	1.2	1.58	0.4	0.53	112	147.42	39	51.33	44	57.92	2.68	3.53	3.62	4.76
74	5/10/83	3.30	m.v.	0.495	67	81.14	0	0	1.1	1.33	0.4	0.48	125	151.38	40	48.44	38	46.02	1.61	1.95	3.02	3.66
75	5/20/83	3.31	9.4	0.470	62	71.29	0	0	0.9	1.03	0.4	0.46	99	113.84	38	43.70	52	59.79	1.71	1.97	3.11	3.58
76	5/31/83	3.15	8.6	0.379	67	62.13	0	0	1.3	1.21	0.2	0.19	100	92.73	48	44.51	58	53.78	2.49	2.31	4.05	3.76
77	6/14/83	3.21	8.9	0.244	74	44.18	0	0	1.0	0.60	0.3	0.18	110	65.67	51	30.45	51	30.45	2.50	1.49	4.98	2.97
78	6/30/83	3.22	8.9	0.163	73	29.11	0	0	1.3	0.52	0.3	0.12	167	66.60	65	25.92	48	19.14	2.10	0.84	5.04	2.01
79	7/16/83	3.24	9.6	0.138	93	31.40	0	0	1.1	0.37	0.3	0.10	156	52.67	61	20.60	70	23.63	2.99	1.01	5.66	1.91
80	8/2/83	3.16	11.7	0.106	94	24.38	0	0	1.1	0.29	0.5	0.13	164	42.53	68	17.64	79	20.49	3.19	0.83	8.68	2.25
81	8/5/83	3.19	m.v.	0.106	83	21.53	0	0	1.0	0.26	0.2	0.05	202	52.39	65	16.86	74	19.19	2.71	0.70	6.96	1.80

Appendix B

ROW	DATE	PH	TEMP	DISCH	ACIDITY	ACIDLD	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
82	8/14/83	3.19	10.0	0.104	93	23.66	0	0	1.3	0.33	0.9	0.23	206	52.42	63	16.03	79	20.10	3.40	0.87	6.76	1.72
	max	3.70	11.7	0.565	151	152.90	0	0	2.0	1.81	1.5	0.62	262	177.07	90	73.32	142	102.37	6.90	3.53	9.44	4.76
	min	3.04	6.2	0.040	42	11.71	0	0	0.3	0.04	0.0	0.00	85	24.20	38	7.05	38	10.08	1.54	0.46	0.70	0.3
	Avg	3.28	8.6	0.216	86	40.25	0	0	1.1	0.59	0.4	0.18	169	77	60	27.5	73.6	32.4	3.2	1.3	5.1	2.1
	Med	3.27	8.6	0.161	85	32.81	0	0	1.1	0.44	0.3	0.13	165	60.08	61	21.71	70	25.7	2.76	1.17	4.8	1.76

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

Arnot 004																						
ROW	DATE	Dischg	pH	TEMP	ACID	ACIDL D	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
1	1/28/80	0.383	3.36	m.v.	76	71.31	0.0	0.0	1.2	1.13	0.8	0.75	143	134.18	m.v.	m.v.	m.v	m.v	m.v	m.v	m.v	m.v
2	2/29/80	0.273	3.32	8.8	152	101.48	0.0	0.0	1.0	0.67	0.4	0.27	160	106.82	m.v.	m.v.	m.v	m.v	m.v	m.v	m.v	m.v
3	3/31/80	0.9	3.46	m.v.	67	147.50	0.0	0.0	1.5	3.30	0.4	0.88	138	303.80	m.v.	m.v.	m.v	m.v	m.v	m.v	m.v	m.v
4	4/22/80	1.646	3.38	8.4	71	285.94	0.0	0.0	1.0	4.03	0.4	1.61	136	547.71	m.v.	m.v.	m.v	m.v	2.06	8.30	4.10	16.51
5	5/10/80	1.745	3.22	8.4	70	298.84	0.0	0.0	0.9	3.84	0.2	0.85	128	546.45	46	196.38	46	196.38	1.94	8.28	4.80	20.49
6	5/31/80	1.255	3.22	8.5	75	230.26	0.0	0.0	0.9	2.76	0.3	0.92	150	460.52	44	135.09	50	153.51	2.09	6.42	4.51	13.85
7	6/18/80	0.9	3.32	8.6	100	220.14	0.0	0.0	0.9	1.98	0.5	1.10	169	377.04	58	127.68	52	114.47	3.00	6.60	7.62	16.78
8	6/30/80	0.446	3.36	8.9	79	86.20	0.0	0.0	0.9	0.98	0.2	0.22	167	182.22	52	56.74	53	57.83	2.35	2.56	7.06	7.70
9	7/19/80	0.319	3.21	8.9	103	80.50	0.0	0.0	0.6	0.47	0.5	0.39	162	126.62	54	42.21	59	46.11	1.96	1.53	3.67	2.87
10	8/12/80	0.241	3.25	8.9	112	65.92	0.0	0.0	1.1	0.65	1.1	0.65	163	95.94	59	34.73	65	38.26	2.54	1.50	5.96	3.51
11	8/27/80	0.209	3.25	9.0	107	54.65	0.0	0.0	1.0	0.51	0.8	0.41	171	87.33	58	29.62	57	29.11	2.38	1.22	5.80	2.96
12	9/11/80	0.178	3.12	9.0	98	42.78	0.0	0.0	1.2	0.52	0.5	0.22	167	72.89	59	25.75	63	27.50	2.36	1.03	7.99	3.49
13	9/27/80	0.136	3.28	8.8	114	37.91	0.0	0.0	1.2	0.40	0.6	0.20	135	44.89	58	19.29	67	22.28	2.63	0.88		2.33
14	10/16/80	0.209	3.16	9.1	118	60.26	0.0	0.0	1.3	0.66	0.6	0.31	186	94.99	61	31.15	72	36.77	3.40	1.74	8.75	4.47
15	11/7/80	0.15	3.32	9.0	115	42.11	0.0	0.0	1.3	0.48	0.4	0.15	230	84.22	62	22.70	94	34.42	4.00	1.46	10.25	3.75
16	11/30/80	0.122	3.29	7.4	131	39.30	0.0	0.0	1.6	0.48	0.4	0.12	242	72.60	65	19.50	82	24.60	2.73	0.82	5.78	1.73
17	12/18/80	0.15	3.17	6.3	130	47.60	0.0	0.0	1.8	0.66	0.5	0.18	206	75.43	79	28.93	73	26.73	5.10	1.87	9.46	3.46
18	1/5/81	0.15	3.29	6.1	137	50.17	0.0	0.0	1.7	0.62	0.5	0.18	251	91.91	62	22.70	109	39.91	4.00	1.47	9.38	3.44
19	1/31/81	0.123	3.11	6.9	122	36.60	0.0	0.0	1.9	0.57	0.4	0.12	181	54.30	60	18.00	102	30.60	6.50	1.95	11.38	3.41
20	2/19/81	0.274	3.40	8.1	88	58.96	0.0	0.0	0.9	0.60	0.2	0.13	132	88.43	50	33.50	73	48.91	1.83	1.23	1.41	0.94
21	3/8/81	0.718	3.35	8.1	70	123.06	0.0	0.0	1.4	2.46	0.1	0.18	160	281.28	44	77.35	58	101.97	2.61	4.59	5.56	9.78
22	3/21/81	0.563	3.33	7.8	80	110.19	0.0	0.0	1.3	1.79	0.2	0.28	145	199.71	40	55.09	75	103.30	1.92	2.64	3.40	4.68
23	4/11/81	0.459	3.41	8.7	78	87.67	0.0	0.0	1.4	1.57	0.3	0.34	169	189.95	53	59.57	67	75.31	2.33	2.62	4.35	4.89
24	4/30/81	0.584	3.41	8.1	140	200.19	0.0	0.0	1.9	2.72	0.3	0.43	177	253.09	52	74.36	54	77.22	2.82	4.03	5.02	7.18
25	5/16/81	0.765	3.44	8.1	168	314.49	0.0	0.0	1.5	2.81	0.3	0.56	147	275.18	48	89.86	68	127.30	1.91	3.58	5.18	9.70
26	5/29/81	0.673	3.32	8.6	77	126.77	0.0	0.0	1.5	2.47	0.2	0.33	121	199.20	52	85.61	48	79.02	2.03	3.34	5.01	8.25
27	6/18/81	0.459	3.39	8.9	72	80.93	0.0	0.0	1.2	1.35	0.2	0.23	193	216.93	56	62.94	67	75.31	2.24	2.52	6.92	7.78
28	6/30/81	0.42	3.35	8.7	82	84.24	0.0	0.0	1.3	1.34	0.2	0.21	166	170.54	51	52.39	56	57.53	2.10	2.16	m.v	m.v
29	7/13/81	0.381	3.36	8.5	111	103.62	0.0	0.0	1.3	1.21	0.5	0.47	159	148.42	50	46.67	64	59.74	2.14	2.00	6.47	3.99
30	7/28/81	0.223	3.31	8.5	103	86.78	0.0	0.0	1.6	1.35	0.4	0.34	143	120.49	52	43.81	82	69.09	2.88	2.43	5.46	4.60
31	8/30/81	0.209	3.28	9.7	100	51.07	0.0	0.0	1.8	0.92	0.5	0.26	198	101.12	55	28.09	63	32.17	3.55	1.81	8.00	4.09
32	9/29/81	0.15	3.10	8.1	111	40.65	0.0	0.0	1.5	0.55	0.4	0.15	185	67.74	58	21.24	103	37.72	4.55	1.67	8.55	3.13
33	10/15/81	0.136	3.00	8.2	124	41.24	0.0	0.0	1.6	0.53	1.4	0.47	211	70.17	64	21.28	92	30.60	4.85	1.61	8.55	2.84
34	10/29/81	0.136	3.19	8.2	137	45.56	0.0	0.0	1.6	0.53	1.1	0.37	222	73.83	57	18.96	110	36.58	4.35	1.45	9.09	3.02
35	11/23/81	0.198	3.19	6.8	126	61.18	0.0	0.0	1.9	0.92	0.5	0.24	235	114.10	58	28.16	96	46.61	4.24	1.06	7.04	3.42
36	12/8/81	0.209	3.19	7.9	133	67.92	0.0	0.0	2.0	1.02	0.5	0.26	221	112.87	56	28.60	77	39.32	4.45	2.27	8.30	4.24
37	12/16/81	0.257	3.15	7.6	121	76.09	0.0	0.0	2.1	1.32	1.1	0.69	204	128.29	54	33.96	83	52.20	3.55	2.23	9.12	5.74
38	1/6/82	0.308	3.16	7.0	131	98.86	0.0	0.0	2.1	1.59	0.6	0.45	196	147.92	53	40.00	74	55.85	4.40	3.32	7.74	5.84
39	1/14/82	0.247	3.46	m.v.	69	64.41	0.0	0.0	2.8	2.61	1.1	1.03	124	115.75	46	42.94	45	42.01	2.10	1.96	0.71	0.66
40	2/23/82	0.5	3.21	7.0	145	177.39	0.0	0.0	1.8	2.20	0.3	0.37	174	212.87	m.v.	m.v.	m.v.	m.v	m.v.	m.v	m.v	m.v

Appendix B

ROW	DATE	Dischg	pH	TEMP	ACID	ACIDL	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
41	3/2/82	0.5	3.17	7.8	97	118.67	0.0	0.0	1.3	1.59	0.4	0.49	168	205.53	49	59.95	70	85.64	1.97	2.41	4.83	4.83
42	3/31/82	1.115	3.30	8.2	73	199.17	0.0	0.0	0.9	2.46	0.4	1.09	140	381.97	46	125.50	59	160.97	1.38	3.77	9.39	9.39
43	5/6/82	0.765	3.40	8.2	65	121.68	0.0	0.0	1.2	2.25	0.8	1.50	144	269.57	49	91.73	42	78.62	1.72	3.22	3.81	7.13
44	5/19/82	0.628	3.25	m.v.	73	112.19	0.0	0.0	1.1	1.69	0.8	1.23	135	207.48	46	70.70	65	99.90	m.v.	m.v	m.v	m.v
45	5/26/82	0.563	3.28	m.v.	64	88.15	0.0	0.0	1.0	1.38	0.3	0.41	125	172.17	48	66.11	64	88.15	1.90	2.62	3.68	5.07
46	6/2/82	0.584	3.27	m.v.	66	94.37	0.0	0.0	0.9	1.29	0.3	0.43	130	185.89	50	71.50	61	87.22	1.85	2.65	4.44	6.35
47	6/10/82	0.971	3.46	m.v.	64	235.27	0.0	0.0	0.9	3.31	0.3	1.10	131	481.57	40	147.04	72	264.68	1.65	6.07	3.64	13.38
48	6/11/82	0.755	3.38	9.0	79	225.82	0.0	0.0	1.1	3.14	0.4	1.14	138	394.47	44	125.77	52	148.64	1.80	5.15	3.81	10.89
49	6/16/82	0.96	3.29	8.8	71	166.80	0.0	0.0	1.1	2.58	0.2	0.47	142	333.60	53	124.51	58	136.26	1.77	4.16	4.02	9.44
50	6/25/82	0.814	3.27	9.0	73	145.14	0.0	0.0	1.1	2.19	0.3	0.60	159	316.12	56	111.34	60	119.29	1.78	3.54	4.06	8.07
51	6/30/82	0.861	3.30	m.v.	69	145.35	0.0	0.0	1.0	2.11	0.4	0.84	145	305.22	45	94.79	63	132.71	1.80	3.79	4.23	8.91
52	7/1/82	0.718	3.34	9.5	64	112.51	0.0	0.0	1.1	1.93	0.3	0.53	103	181.08	51	89.66	42	73.84	1.76	3.09	4.20	7.38
53	7/8/82	0.656	3.31	8.0	66	105.93	0.0	0.0	1.1	1.77	0.2	0.32	140	224.69	52	84.36	43	69.01	2.01	3.23	3.93	6.31
54	7/16/82	0.534	3.39	9.2	74	96.68	0.0	0.0	0.7	0.91	0.3	0.39	137	178.99	54	70.55	47	61.40	1.90	2.48	4.30	6.27
55	7/28/82	0.441	3.32	9.7	81	87.39	0.0	0.0	0.9	0.97	0.3	0.32	145	156.43	54	58.26	43	46.39	2.90	2.05	5.06	5.46
56	8/6/82	0.397	3.28	m.v.	64	62.16	0.0	0.0	0.9	0.87	0.3	0.29	153	148.61	50	48.56	60	58.28	2.09	2.03	5.62	5.46
57	8/12/82	0.366	3.20	9.0	96	85.96	0.0	0.0	0.9	0.81	0.3	0.27	200	179.09	m.v.	m.v.	m.v.	m.v	2.04	1.83	5.26	4.71
58	8/17/82	0.344	3.28	m.v.	72	60.60	0.0	0.0	0.8	0.67	0.0	0.00	168	141.39	55	46.29	60	50.50	2.17	1.83	m.v	m.v
59	8/26/82	0.289	3.24	9.4	80	56.57	0.0	0.0	0.8	0.57	0.4	0.28	175	123.64	72	50.91	51	36.06	2.46	1.74	6.15	4.35
60	9/12/82	0.231	3.22	10.3	100	56.52	0.0	0.0	0.8	0.45	0.8	0.45	187	105.69	52	29.39	75	42.39	2.69	1.52	6.96	3.93
61	10/2/82	0.173	3.21	10.7	115	48.67	0.0	0.0	1.1	0.47	0.1	0.04	256	108.35	63	26.67	63	26.67	2.79	1.18	8.03	3.40
62	10/16/82	0.16	3.91	9.2	136	53.24	0.0	0.0	1.3	0.51	0.4	0.16	184	72.03	60	23.49	86	33.67	3.04	1.19	8.40	3.29
63	10/30/82	0.158	3.18	9.7	124	47.93	0.0	0.0	0.6	0.23	0.3	0.12	219	84.66	63	24.35	75	28.99	3.18	1.23	9.57	3.70
64	11/5/82	0.139	3.14	m.v.	121	41.15	0.0	0.0	0.6	0.20	0.1	0.03	221	75.16	62	21.08	101	34.35	3.27	1.11	m.v	m.v
65	11/24/82	0.133	3.12	7.8	132	42.95	0.0	0.0	1.2	0.39	0.2	0.07	m.v.	m.v.	60	19.52	99	32.21	3.83	1.25	9.40	3.06
66	12/16/82	0.135	3.18	8.3	127	41.95	0.0	0.0	1.5	0.50	0.5	0.17	268	88.52	65	21.47	102	33.69	3.72	1.23	12.90	4.26
67	1/8/83	0.186	3.13	6.9	112	50.97	0.0	0.0	1.5	0.68	0.3	0.14	262	119.23	61	27.76	103	46.87	3.61	1.64	13.50	6.14
68	2/5/83	0.295	3.12	6.4	125	90.22	0.0	0.0	1.9	1.37	0.8	0.58	200	144.35	65	46.91	67	48.36	3.40	2.45	13.56	9.79
69	3/1/83	0.351	3.17	m.v.	115	100.47	0.0	0.0	1.6	1.37	0.6	0.52	227	194.94	62	53.24	80	68.70	3.09	2.65	9.05	7.77
70	4/6/83	0.979	3.20	8.3	95	227.54	0.0	0.0	1.7	4.07	0.3	0.72	166	397.60	49	117.37	74	177.25	1.20	2.87	4.26	10.20
71	4/23/83	1.501	3.23	8.6	77	282.77	0.0	0.0	1.3	4.77	0.3	1.10	213	782.21	44	161.58	17	62.43	2.72	9.99	5.30	19.46
72	5/5/83	1.838	3.13	8.4	128	575.59	0.0	0.0	2.1	9.44	0.7	3.15	207	930.84	39	175.38	54	242.83	3.40	15.29	6.15	27.66
73	5/10/83	1.574	3.29	m.v.	67	258.01	0.0	0.0	1.0	3.85	0.3	1.16	100	385.09	39	150.19	51	196.40	2.03	7.82	4.25	16.37
74	5/20/83	1.358	3.94	8.9	62	205.99	0.0	0.0	0.8	2.66	0.2	0.66	86	285.73	39	129.58	74	145.86	1.98	6.58	4.28	14.22
75	5/31/83	1.07	3.17	8.3	67	175.40	0.0	0.0	1.0	2.62	0.1	0.26	150	392.68	49	128.27	56	146.60	2.62	6.86	4.92	12.88
76	6/14/83	0.787	3.25	8.6	74	142.48	0.0	0.0	0.9	1.73	0.2	0.39	148	284.97	48	92.42	48	92.42	2.18	4.20	5.90	11.36
77	6/30/83	0.587	3.28	9.0	73	104.84	0.0	0.0	0.9	1.29	0.2	0.29	152	218.29	69	99.09	50	71.81	2.12	3.04	5.10	7.32
78	7/16/83	0.488	3.30	9.6	92	109.84	0.0	0.0	1.0	1.19	0.3	0.36	160	191.03	56	66.86	92	109.84	2.43	2.90	6.04	7.21
79	8/2/83	0.417	3.18	9.4	97	98.96	0.0	0.0	1.0	1.02	0.3	0.31	167	170.38	66	67.34	65	66.31	2.59	2.64	6.92	7.06
80	8/5/83	0.403	3.23	m.v.	83	81.84	0.0	0.0	1.0	0.99	0.2	0.20	224	220.86	61	60.14	64	63.10	2.80	2.76	7.39	7.29
81	8/14/83	0.362	3.23	9.4	100	88.57	0.0	0.0	1.2	1.06	0.2	0.18	202	178.90	60	53.14	69	61.11	2.71	2.40	9.40	8.33

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	Dischg	pH	TEMP	ACID	ACIDL	ALK	ALKLD	TFE	TFELD	FE	FELD	SO4	SO4LD	CA	CALD	MG	MGLD	MN	MNLD	AL	ALLD
	max	1.84	3.94	10.70	168.00	575.59	0.00	0.00	2.80	9.44	1.40	3.15	268.00	930.84	79.00	196.38	110.00	264.68	6.50	15.29	13.56	27.66
	min	0.12	3.00	6.10	62.00	36.60	0.00	0.00	0.60	0.20	0.00	0.00	86.00	44.89	39.00	18.00	17.00	22.28	1.20	0.82	0.71	0.66
	Avg	0.53	3.28	8.47	96.99	115.40	0.00	0.00	1.26	1.60	0.42	0.49	171.80	210.83	54.29	65.17	67.68	76.74	2.71	3.09	6.45	7.17
	Med	0.40	3.28	8.60	96.00	88.15	0.00	0.00	1.20	1.29	0.30	0.36	166.50	175.54	54.00	53.24	65.00	61.11	2.45	2.44	5.85	5.84

APPENDIX - C

Clarion Discharge Data

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

CLARION ROW	DATE	pH	DISCH	ACID	TOT. FE	FFE	SO ₄
1	2/16/82	3.38	-	189	14.0	9.0	344
2	3/17/82	3.51	-	139	9.8	8.7	296
3	3/30/82	2.90	10.32	1102	33.5	32.1	1611
4	4/12/82	3.13	40.84	607	38.6	27.8	1002
5	4/22/82	2.83	9.43	1038	83.2	30.5	1401
6	5/11/82	2.95	3.59	719	73.9	17.1	1681
7	5/26/82	2.77	9.43	644	85.7	32.6	1406
8	6/9/82	2.78	5.39	793	85.0	32.4	1748
9	6/23/82	3.19	3.60	943	94.6	55.8	1350
10	7/7/82	2.74	0.20	1197	108.0	50.6	1935
11	7/21/82	2.74	3.60	951	97.1	41.9	2064
12	8/3/82	2.83	12.21	708	111.0	61.0	1656
13	8/30/82	2.95	0.45	819	90.0	29.5	1436
14	9/17/82	3.22	0.45	480	72.0	60.6	1114
15	9/27/82	3.20	6.70	317	32.5	0.9	880
16	10/12/82	3.11	1.35	411	46.4	8.6	1294
17	10/26/82	3.17	0.20	441	60.0	22.5	2861
18	11/8/82	3.14	3.60	401	16.0	12.0	1068
19	11/24/82	3.27	14.80	299	45.0	30.6	797
20	12/28/82	3.15	22.00	495	85.5	56.5	1462
21	1/12/83	3.16	9.40	910	182.0	112.0	2436
22	1/26/83	3.12	8.50	985	185.0	101.0	2203
23	2/9/83	3.16	3.60	968	174.0	116.0	1844
24	2/23/83	3.04	5.40	744	129.0	42.0	1355
25	3/9/83	3.04	4.00	850	129.0	34.0	1619
26	4/5/83	3.12	8.50	630	133.0	43.0	1488
27	4/19/83	3.01	9.40	598	137.0	86.0	1870
28	5/10/83	2.94	7.63	990	165.0	69.0	2397
29	5/24/83	2.95	20.20	795	131.0	86.0	1934
30	6/15/83	2.67	0.17	1247	136.0	66.7	2134
31	7/6/83	2.78	4.04	1383	215.0	92.3	3241
32	7/19/83	2.78	2.70	1205	257.0	105.0	2216
33	8/10/83	3.03	5.40	954	182.0	93.0	2275
34	8/23/83	2.88	0.10	985	174.0	119.0	2682
35	9/7/83	2.92	3.60	469	98.4	43.3	1175
36	10/13/83	3.03	5.40	663	102.0	47.0	1652
37	10/26/83	2.76	6.70	636	86.4	25.0	1642
38	11/9/83	3.00	1.30	584	112.0	26.5	1623
39	11/21/83	3.25	12.60	201	73.5	50.0	859
40	12/8/83	3.29	14.60	570	115.0	89.0	1193

Appendix C

ROW	DATE	pH	DISCH	ACID	TOT. FE	FFE	SO ₄
41	12/20/83	3.18	9.40	992	194.0	136.0	2000
42	1/5/84	3.26	12.21	954	153.0	131.0	2002
43	1/27/84	5.23	-	528	86.0	32.0	1316
44	2/15/84	3.27	-	451	70.0	22.0	1178
45	2/28/84	3.24	-	746	108.0	66.5	1757
46	3/19/84	3.16	-	518	86.0	47.0	1372
47	3/27/84	3.04	-	588	91.0	32.0	1544
48	4/12/84	2.90	-	682	90.0	27.5	1722
49	4/25/84	3.06	-	386	24.0	4.5	839
50	5/8/84	3.03	-	487	67.6	17.0	1250
51	5/22/84	3.09	6.30	359	36.5	25.5	708
52	6/6/84	3.29	6.70	234	54.0	39.0	1367
53	6/27/84	5.68	36.30	255	75.0	73.5	1837
54	7/11/84	5.28	30.50	147	45.0	40.0	980
55	8/8/84	4.66	20.20	416	134.0	132.0	1822
56	8/21/84	5.58	-	182	75.0	55.0	2064
57	9/5/84	6.03	-	19	38.5	33.5	1753
58	10/3/84	4.52	-	265	58.0	46.5	1501
59	10/16/84	4.05	4.00	176	36.0	17.0	1672
60	11/1/84	4.49	5.40	160	27.0	21.0	1572
61	11/14/84	4.70	14.80	175	43.0	36.5	1624
62	11/28/84	5.76	83.93	46	25.0	10.0	556
63	12/12/84	4.79	2.69	160	48.6	41.4	721
64	12/27/84	5.23	36.36	50	20.0	15.6	426
65	1/10/85	4.66	-	378	106.0	97.0	1701
66	2/27/85	4.60	-	289	69.0	64.0	1082
67	3/12/85	5.11	-	60	22.0	9.0	356
68	3/24/85	4.23	-	306	46.0	46.0	1322
69	4/10/85	3.75	28.56	232	36.0	32.2	975
70	4/23/85	3.03	5.39	444	28.0	32.0	1881
71	4/24/85	3.75	28.56	23.2	36.0	32.2	975
72	5/2/85	3.16	6.23	499	78.5	59.0	1843
73	5/22/85	3.06	4.13	1546	62.0	27.0	1280
74	6/4/85	4.35	6.83	489	50.0	23.5	1960
75	7/1/85	5.25	172.00	147	12.5	12.5	17056
76	7/18/85	4.78	0.39	121	11.5	9.0	1580
77	7/31/85	5.33	5.37	164	133.0	33.9	1735
78	8/13/85	6.18	0.05	2	54.0	11.0	1313
79	8/28/85	6.43	0.09	1	102.0	12.0	941
80	9/10/85	6.12	14.82	17	8.7	7.8	617

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	pH	DISCH	ACID	TOT. FE	FFE	SO₄
81	9/24/85	5.35	1.83	109	22.7	19.8	1528
82	10/22/85	4.88	12.21	165	29.0	27.0	1192
83	11/7/85	4.61	0.95	298	74.0	67.4	1029
84	11/19/85	4.02	9.13	327	76.5	73.5	1284
85	12/4/85	3.58	10.37	419	84.0	75.5	1566
86	12/18/85	3.68	12.48	592	116.0	114.0	1948
87	1/9/86	3.47	4.13	1080	146.0	143.0	2495
88	1/21/86	3.94	7.63	343	62.0	62.0	1258
89	2/3/86	3.69	14.82	370	70.0	64.0	1720
90	2/18/86	4.32	50.54	80	20.6	8.4	364
91	3/4/86	3.40	21.79	516	85.0	62.0	1501
92	4/1/86	2.87	5.40	648	118.0	104.0	2180
93	5/5/86	2.90	3.08	678	74.1	32.0	2100
94	6/2/86	3.00	2.62	508	66.5	30.1	2210
95	7/7/86	3.00	1.21	574	30.5	12.2	2130
96	8/4/86	2.90	12.21	478	96.7	73.0	2120
	max	6.43	172.00	1546.00	257.00	143.00	3241.00
	min	2.67	0.05	1.00	8.70	0.90	296.00
	Avg	3.70	12.57	522.38	82.40	48.38	1528.30
	Med	3.20	6.70	483.50	75.00	37.75	1569.00

APPENDIX - D

Ernest Discharge Data

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ERNEST ROW	DATE	DAYS	PH	FLOW	ACID	ACIDL D	FE	FELD	FFE	SO₄	SO₄LD
1	3/19/81	0	2.63	55	5219	3444	461	304	452	5410	3571
2	3/27/81	8	2.71	288	5111	17663	447	1544	440	5135	17746
3	3/30/81	11	2.67	229	4986	13701	444	1220	428	5174	14218
4	7/30/81	133	2.50	42	3082	1553	360	181	348	4445	2240
5	8/7/81	141	2.55	39	3564	1668	489	229	320	3552	1662
6	8/13/81	147	2.45	28	3716	1248	459	154	357	3981	1338
7	8/21/81	155	2.48	17	4070	830	500	102	410	4742	967
8	8/26/81	160	2.35	12	4314	621	619	89	419	3716	525
9	9/4/81	169	2.62	340	2165	8833	290	1183	177	3107	12676
10	9/18/81	183	2.53	47	3819	2153	391	221	184	3677	2074
11	9/30/81	195	2.36	20	4293	1030	519	125	399	2434	584
12	10/9/81	204	2.48	15	4267	768	584	105	339	5343	962
13	10/21/81	216	2.42	12	4900	706	674	97	450	4942	712
14	11/4/81	230	2.46	76	4300	3922	530	483	364	2304	2101
15	11/16/81	242	2.36	32	4698	1804	618	237	387	4842	1859
16	11/30/81	256	2.54	47	4375	2468	486	274	267	4977	2807
17	1/12/82	299	2.69	56	3592	2414	518	348	396	3963	2663
18	1/19/82	306	2.58	47	3858	2178	653	368	408	4031	2273
19	2/1/82	319	2.80	113	2470	3349	366	499	330	1873	2540
20	2/8/82	326	2.43	199	3940	9409	538	1285	520	2804	6696
21	2/23/83	341	2.62	189	2892	6559	463	1050	335	2573	5836
22	3/2/82	348	2.60	208	3004	7497	525	1310	438	3043	7595
23	3/17/82	363	2.54	340	3044	12419	594	2424	485	3025	12342
24	3/30/82	376	2.67	288	2757	9528	639	2208	556	2956	10216
25	5/3/82	410	2.60	94	2809	3169	705	795	642	2951	3329
26	5/10/82	417	2.63	81	2665	2590	694	675	634	2791	2713
27	5/17/82	424	2.63	51	3043	1962	660	403	576	3161	1935
28	5/24/82	431	2.54	42	2855	1439	615	310	518	4002	2017
29	6/8/82	446	2.58	113	2292	3108	278	377	160	2797	3793
30	6/21/82	459	2.55	42	2499	1259	377.2	190	221	2476	1248
31	6/28/82	466	2.49	51	2349	1438	362	222	226	2834	1734
32	7/12/82	480	2.50	39	3455	1617	540	253	319	3794	1776
33	7/19/82	487	2.53	28	3567	1199	596	200	393	4003	1345
34	7/26/82	494	2.48	17	4456	909	694	142	507	4593	937
35	8/2/82	501	2.42	15	4591	826	693	125	470	5125	923
36	8/9/82	508	2.30	6	4589	330	624	45	268	4395	316
37	8/16/82	515	2.26	3.5	4639	195	495	21	118	5208	219
38	8/23/82	522	2.24	3.5	4670	196	540	23	107	5803	244
39	8/31/82	530	2.27	3	5606	202	540	19	132	5114	184
40	1/3/83	655	2.30	3	4306	155	330	12	89	4617	166

Appendix D

ROW	DATE	DAYS	PH	FLOW	ACID	ACIDL D	FE	FELD	FFE	SO ₄	SO ₄ LD
41	1/10/83	662	2.40	7	3247	273	276	23	44	3570	300
42	1/17/83	669	2.30	4	4188	201	308	15	30	4256	205
43	2/14/83	697	2.40	8	3105	298	314	30	152	3159	304
44	2/22/83	705	2.50	8	3455	332	353	34	156	3666	352
45	2/28/83	711	2.30	7	3620	305	412	35	182	4298	362
46	3/8/83	719	2.50	15	3545	639	352	63	150	3630	654
47	3/14/83	725	2.40	8	1744	168	400	38	168	2650	255
48	3/22/83	733	2.40	26	2356	736	264	82	122	2860	894
49	3/28/83	739	2.50	75	1273	1147	306	276	121	2348	2116
50	4/4/83	746	2.50	56	1478	995	354	238	142	1619	1089
51	4/11/83	753	2.50	88	1620	1713	381	403	149	2369	2505
52	4/25/83	767	2.50	136	3109	5081	476	778	260	3104	5073
53	5/4/83	776	2.50	179	2872	6178	638	1372	448	3570	7679
54	5/9/83	781	2.50	199	3293	7875	780	1865	478	3745	8955
55	5/18/83	790	2.60	179	3866	8316	895	1925	792	4223	9084
56	5/23/83	795	2.60	252	2690	8146	705	2135	600	2820	8539
57	5/31/83	803	2.60	240	3028	8733	740	2134	700	4321	12461
58	6/7/83	810	2.60	161	3300	6384	820	1586	710	3867	7981
59	6/15/83	818	2.60	152	3060	5589	808	1476	659	2909	5313
60	6/20/83	823	2.60	113	2980	4046	845	1147	659	3260	4427
61	6/27/83	830	2.60	100	3195	3839	659	792	579	3338	4011
62	7/6/83	839	2.60	56	3893	2680	760	511	536	3681	2477
63	7/11/83	844	2.50	35	3350	1409	702	295	468	3256	1369
64	7/18/83	851	2.50	17	3706	758	630	129	435	4088	835
65	7/25/83	858	3.10	17	3559	727	536	109	311	3682	752
66	8/1/83	865	2.40	8	4045	4045	389	54	334	4288	412
67	8/8/83	872	2.10	4	4368	210	456	22	70	5621	270
68	8/15/83	879	2.30	4	4956	238	478	23	80	5283	254
69	8/22/83	886	2.30	3	4293	155	483	17	688	6115	220
70	8/29/83	893	2.20	7	4619	389	462	89	79	5347	450
71	9/6/83	901	2.20	4	4881	235	515	25	79	5389	259
72	9/12/83	907	2.30	8	5113	492	561	54	848	5141	494
73	9/19/83	914	2.30	4	4820	232	510	25	820	5982	288
74	9/26/83	921	2.30	4	4749	200	527	22	700	6014	253
75	10/3/83	928	2.30	3	4953	179	530	19	580	5932	214
76	10/11/83	936	2.30	6	5367	387	540	39	760	5738	414
77	10/17/83	942	2.30	8	4978	479	528	51	860	5657	544
78	10/24/83	949	2.30	4	4891	235	415	20	315	4896	235
79	10/31/83	956	2.30	4	4295	206	430	21	412	4953	238
80	11/14/83	970	2.30	6	3964	286	395	28	183	4459	321
81	11/21/83	977	2.40	6	3616	261	365	26	210	4812	347

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	PH	FLOW	ACID	ACIDL D	FE	FELD	FFE	SO ₄	SO ₄ LD
82	11/29/83	985	2.40	23	2077	574	216	60	240	2329	644
83	12/5/83	991	2.70	81	1130	110	93	91	190	1139	1109
84	12/13/83	999	2.60	129	2664	4130	272	422	816	2686	4164
85	12/19/83	1005	2.50	100	2849	3424	278	334	1000	3080	3701
86	12/27/83	1013	2.50	12	3281	473	404	58	1760	3658	527
87	1/3/84	1020	2.60	40	3916	1882	778	373	332	4724	2271
88	1/17/84	1034	2.60	85	5084	5193	855	873	798	5685	5807
89	1/23/84	1040	2.60	50	4954	2977	815	490	810	5211	3131
90	1/30/84	1047	2.60	100	4685	5630	820	985	820	4958	5958
91	2/6/84	1054	2.60	81	4799	4671	1120	1090	765	4869	4739
92	2/13/84	1061	2.60	80	3431	3298	700	673	480	3491	3356
93	2/21/84	1069	2.60	190	3317	7573	530	1210	335	3831	8747
94	2/27/84	1075	2.60	50	3250	2977	520	490	290	3532	3131
95	3/5/84	1082	2.70	170	2619	5350	544	1111	376	2928	5981
96	3/12/84	1089	2.50	152	3255	5945	630	1150	430	4645	8484
97	3/19/84	1096	2.60	170	3190	6516	815	1665	550	4112	8400
98	3/26/84	1103	2.70	189	3633	8251	840	1908	620	4030	9153
99	4/2/84	1110	2.50	200	3336	8027	720	1730	570	3416	8210
100	4/12/84	1120	2.60	288	3259	11279	685	2371	455	3266	11303
101	4/16/84	1124	2.60	263	3176	10037	675	2133	490	3243	10249
102	4/23/84	1131	2.60	288	2601	9001	625	2165	450	2872	9939
103	4/30/84	1138	2.70	300	2600	9373	660	2379	505	2880	10382
104	5/7/84	1145	2.70	275	2947	9739	725	2396	590	3135	10360
105	5/14/84	1152	2.70	300	3088	11132	625	2758	625	3490	12581
106	5/21/84	1159	2.60	251	2709	8171	720	2172	455	3112	9386
107	5/29/84	1167	2.80	350	1905	8012	455	1914	400	1938	8151
108	6/4/84	1173	2.60	313	2713	10204	540	2031	425	3203	12047
109	6/11/84	1180	2.60	198	2349	5589	635	1511	405	2710	6448
110	6/19/84	1188	2.80	345	1369	5676	245	1016	180	1538	6376
111	6/25/84	1194	2.60	320	3761	11462	395	1519	337	3933	15124
112	7/2/84	1201	2.60	189	3241	7361	454	1238	375	3285	7461
113	7/9/84	1208	2.60	199	3110	7437	596	1425	436	3349	8008
114	7/16/84	1215	2.60	198	3014	7171	605	1439	520	3399	8087
115	7/30/84	1229	2.60	128	3480	5353	695	1069	590	3680	5660
116	8/6/84	1236	2.70	100	3071	3690	653	785	575	3481	4183
117	8/13/84	1243	2.90	100	778	935	94	113	56	785	943
118	8/20/84	1250	2.60	350	3236	350	425	1787	270	3513	14775
119	8/27/84	1257	2.50	200	2815	6765	468	1125	298	3562	8561
120	9/4/84	1265	2.50	88	3611	3818	490	518	300	3821	4041
121	9/10/84	1271	2.50	76	3521	3216	460	420	432	4681	4275

Appendix D

ROW	DATE	DAYS	PH	FLOW	ACID	ACIDL	FE	FELD	FFE	SO ₄	SO ₄ LD
122	9/17/84	1278	2.50	60	4054	2923	705	508	525	4270	3079
123	9/24/84	1285	2.60	65	4057	3169	20	797	530	4738	3701
124	10/1/84	1292	2.50	46	4596	2541	890	492	660	4839	2675
125	10/9/84	1300	2.50	30	4467	1074	900	216	670	4813	1157
126	10/16/84	1307	2.50	10	4471	537	810	97	510	5206	626
127	10/22/84	1313	2.40	15	3552	640	470	85	220	4092	738
128	10/29/84	1320	2.40	4	4263	205	516	25	506	5339	257
129	11/7/84	1329	2.30	4	3909	188	440	21	63	4583	220
130	11/13/84	1335	2.30	8	3298	317	396	38	100	4391	422
131	11/19/84	1341	2.30	8	3944	379	374	36	86	4362	419
132	11/29/84	1351	2.40	13	3315	518	414	65	117	3825	598
133	12/5/84	1358	2.40	6	4370	315	322	23	82	4424	319
134	12/10/84	1363	2.50	15	3685	664	310	56	86	3598	649
135	12/17/84	1370	3.10	20	2599	625	326	78	96	3136	754
136	1/3/85	1387	2.50	161	3017	5841	454	879	246	3586	6942
137	1/7/85	1391	2.50	100	3301	3967	568	683	334	3459	4157
138	1/17/85	1401	2.40	88	4121	4359	684	724	422	4293	4541
139	2/26/85	1441	2.70	51	1790	1097	310	190	170	1930	1183
140	3/4/85	1447	2.60	66	3364	2669	418	332	218	3834	3042
141	3/13/85	1456	2.50	46	3462	1914	390	216	210	3576	1977
142	3/19/85	1462	2.60	3003	1697	420	237	168	95	3585	2025
143	3/26/85	1469	2.50	3188	16401	375	1929	184	182	3409	17538
144	4/1/85	1475	2.70	470	2045	11553	306	1729	182	2116	11954
145	4/8/85	1482	2.50	251	3534	10662	536	1617	370	3671	11075
146	4/16/85	1490	2.60	161	3574	6916	650	1258	505	3745	7247
147	4/22/85	1496	2.50	179	4465	9607	725	1560	510	4625	9951
148	4/29/85	1503	2.70	199	3956	9463	815	1949	736	4333	10364
149	5/14/85	1518	2.60	128	3290	5062	863	1328	638	3666	5640
150	5/25/85	1529	2.60	152	3194	5836	751	1372	551	3205	5856
151	5/29/85	1533	2.60	51	3440	2109	675	414	480	3511	2151
152	6/4/85	1539	2.60	56	3042	2048	575	387	425	3143	2116
153	6/11/85	1546	2.50	42	2884	1456	470	237	270	3010	1520
154	6/18/85	1553	2.50	7	3427	288	540	45	175	3814	321
155	6/24/85	1559	2.40	12	3787	546	555	80	230	4950	714
156	7/2/85	1567	2.40	17	3635	743	495	101	162	3925	802
157	7/8/85	1573	2.40	6	3966	286	425	31	134	4532	327
158	7/17/85	1582	2.30	10	3880	466	335	24	36	4321	519
159	7/23/85	1588	2.30	7	3976	335	356	30	52	4660	392
160	7/30/85	1595	2.30	10	4076	490	395	47	17	5267	634
161	8/7/85	1603	2.50	2	4626	111	384	10	8	4864	117

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	PH	FLOW	ACID	ACIDL D	FE	FELD	FFE	SO₄	SO₄LD
162	8/27/85	1623	2.30	3	4657	168	406	15	11	5262	190
163	9/5/85	1632	2.30	3	4040	146	420	15	8	5356	193
164	9/12/85	1639	2.30	3	5141	185	428	15	14	5334	192
165	9/18/85	1645	2.30	4	4598	182	398	16	11	5015	199
166	9/25/85	1652	2.30	3	4441	160	378	14	13	4649	168
167	10/16/85	1673	2.50	2	4658	112	410	10	27	5812	140
168	10/30/85	1687	2.50	2	4805	116	403	10	20	5676	136
169	11/5/85	1693	2.40	4	4350	209	410	20	13	4857	117
170	11/13/85	1701	2.60	35	1714	721	116	49	20	1870	787
171	11/20/85	1708	2.50	94	1781	2012	113	128	9	1962	2217
172	12/4/85	1722	2.40	251	3136	9461	385	1162	163	3313	9995
173	12/10/85	1728	2.60	81	2947	2869	376	366	146	142	3062
174	12/17/85	1735	2.50	313	3166	11911	584	2197	400	3689	13879
		max	3.10	3188	16401	17663	1929	2758	1760	6115	17746
		min	2.10	2	778	111	20	10	8	142	117
		Avg	2.51	127.23	3621.0	3367	527	627	365	3887	3840
		Med	2.50	51	3539.5	1843	513	275	361	3804	2109

APPENDIX - E

Fisher Discharge Data

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

FISHER ROW	DATE	DAYS	FLOW	ACID	SO₄	FE	MN	AL
1	11/27/81	0	50.0	127.0	490	4.00	11.70	-
2	3/11/82	104	75.0	209.0	1100	4.40	25.10	-
3	5/19/82	173	130.0	210.0	550	7.00	33.00	8.00
4	6/9/82	194	273.0	86.9	248	1.06	6.84	20.50
5	6/22/82	207	87.0	105.0	440	3.50	9.44	3.50
6	7/29/82	244	54.0	174.0	290	3.84	8.94	29.50
7	8/20/82	266	30.0	119.0	280	3.32	9.44	6.75
8	8/26/82	272	30.0	125.0	300	4.12	9.44	8.75
9	9/18/82	295	20.0	105.0	370	4.50	10.50	6.30
10	10/9/82	316	30.0	127.0	370	5.30	9.44	6.00
11	11/13/82	351	18.1	138.0	440	4.80	12.10	0.32
12	12/11/82	379	36.8	120.0	410	2.83	9.47	9.20
13	1/22/83	421	30.0	112.0	310	3.10	8.03	5.10
14	2/14/83	444	64.0	108.0	210	2.21	6.99	1.09
15	5/18/83	537	100.0	98.6	220	2.12	6.08	0.50
16	8/17/83	628	44.9	126.0	160	2.56	7.19	3.23
17	8/24/83	635	33.0	107.0	240	0.79	8.15	4.27
18	11/22/83	725	115.0	144.0	430	2.23	9.68	2.75
19	12/15/83	748	614.0	107.0	176	0.99	4.98	0.50
20	12/17/83	750	273.0	93.1	120	1.65	3.78	0.50
21	1/28/84	792	54.0	111.0	260	2.46	7.58	0.50
22	3/2/84	826	100.0	101.0	220	1.13	5.91	1.59
23	3/31/84	855	204.0	146.0	410	1.46	11.80	2.41
24	4/21/84	876	483.0	237.0	1200	4.30	25.40	3.47
25	5/26/84	911	100.0	118.0	280	1.40	8.81	2.52
26	6/27/84	943	87.0	182.0	190	1.62	8.10	1.98
27	7/25/84	971	44.9	149.0	190	1.49	7.72	2.24
28	8/21/84	998	122.0	149.0	120	1.34	7.42	1.78
29	9/6/84	1014	69.0	141.0	300	1.42	9.49	2.78
30	9/21/84	1029	37.0	83.6	49	2.01	10.90	3.10
31	10/3/84	1041	-	70.4	350	1.81	12.10	4.02
32	10/16/84	1054	-	68.3	410	1.22	12.60	4.46
33	10/23/84	1061	21.0	64.2	410	1.09	12.60	3.77
34	10/24/84	1062	-	80.4	460	1.14	12.70	3.77
35	10/29/84	1067	30.0	80.4	440	1.56	15.40	4.45
36	11/23/84	1092	18.0	87.7	550	2.37	15.90	7.56
37	12/18/84	1117	130.0	55.1	320	0.86	10.40	4.05
38	1/26/85	1156	27.0	41.8	230	1.01	6.08	1.92
39	2/23/85	1184	81.0	51.0	272	1.21	7.00	3.58
40	3/11/85	1200	64.0	28.6	292	0.98	7.08	2.61

Appendix E

ROW	DATE	DAYS	FLOW	ACID	SO ₄	FE	MN	AL
41	3/20/85	1209	69.0	53.0	272	1.01	7.35	2.29
42	3/29/85	1218	107.0	42.8	280	1.57	8.42	2.96
43	4/10/85	1230	122.0	53.0	256	1.11	7.36	2.89
44	4/17/85	1237	73.0	67.2	280	1.40	8.77	3.59
45	4/24/85	1244	45.0	57.3	300	1.42	8.89	3.23
46	5/1/85	1251	30.0	63.2	300	1.03	9.30	3.16
47	5/10/85	1260	69.0	45.4	290	1.49	9.65	2.56
48	5/16/85	1266	-	38.0	342	0.90	9.16	1.57
49	5/22/85	1272	18.0	51.4	320	1.33	10.10	4.27
50	5/28/85	1278	69.0	79.0	332	1.25	11.70	3.77
51	6/1/85	1282	174.0	86.9	280	1.24	12.00	3.82
52	6/26/85	1307	45.0	61.2	240	1.90	10.60	2.47
53	7/24/85	1335	54.0	79.0	310	1.33	12.70	3.95
54	8/19/85	1361	18.0	73.1	450	1.20	13.60	4.49
55	9/21/85	1394	24.0	57.1	380	0.82	11.70	2.98
56	10/26/85	1429	9.7	57.1	370	0.72	9.06	2.90
57	11/18/85	1452	299.0	51.2	332	0.90	9.36	3.35
58	11/23/85	1457	87.0	49.2	300	1.02	7.82	4.44
59	12/23/85	1487	64.0	47.3	290	1.17	9.19	3.94
60	1/18/86	1513	18.0	53.2	270	1.18	9.55	5.87
61	2/17/86	1543	54.0	53.2	260	0.86	4.95	2.15
62	3/22/86	1576	448.0	27.6	800	0.49	10.20	4.51
63	4/10/86	1595	75.0	49.3	830	0.28	11.40	4.99
64	5/17/86	1632	30.0	62.0	410	0.32	7.37	6.05
65	6/10/86	1656	33.0	35.3	510	0.05	7.82	4.60
66	7/15/86	1691	18.0	58.8	430	0.26	7.46	13.30
67	8/12/86	1719	18.0	56.8	710	0.44	5.85	6.50
68	9/13/86	1751	14.0	58.8	424	0.25	6.77	5.79
69	10/10/86	1778	45.0	54.9	368	0.20	5.79	6.08
70	11/15/86	1814	100.0	45.1	300	0.54	3.99	1.78
71	12/13/86	1842	130.0	47.0	324	0.49	4.63	0.50
72	1/17/86	1877	204.0	60.8	810	0.25	8.24	0.50
73	2/14/87	1905	75.0	51.0	950	0.21	10.10	4.68
74	3/14/87	1933	75.0	51.0	750	0.42	8.13	5.12
75	4/11/87	1961	130.0	34.2	368	0.31	4.21	1.00
76	5/9/87	1989	64.0	48.9	460	0.40	5.57	1.95
77	6/13/87	2024	23.0	39.1	444	0.29	4.24	3.25
78	7/14/87	2055	45.0	37.1	390	0.28	4.78	3.77
79	8/12/87	2084	0.0	34.4	356	0.11	4.47	1.68
		max	614.0	237.0	1200.0	7.00	33.00	29.50

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	FLOW	ACID	SO₄	FE	MN	AL
		min	0.0	27.6	49.0	0.05	3.78	0.32
		Avg	90.1	84.3	382.2	1.60	9.46	4.23
		Med	64.0	67.2	324.0	1.21	8.94	3.50

APPENDIX - F

Markson Discharge Data

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

MARKSON											
ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO ₄	FE++	AL Load
1	7/30/81	0	-	3.40	136	38.900	-	-	407	32.30	-
2	8/6/81	7	-	3.28	144	43.500	-	-	390	40.30	-
3	8/13/81	14	-	3.35	30	43.900	-	-	353	41.60	-
4	9/10/81	42	-	3.22	129	50.000	-	-	398	45.30	-
5	9/17/81	49	-	3.00	130	43.900	5.320	2.580	325	48.40	-
6	9/24/81	56	-	3.30	114	11.200	5.320	2.850	360	11.00	-
7	10/1/81	63	-	3.30	214	49.100	5.320	3.050	400	51.00	-
8	10/8/81	70	-	3.20	94	46.400	5.300	2.170	370	58.00	-
9	10/15/81	77	-	3.30	104	46.500	5.230	1.900	365	61.00	-
10	10/22/81	84	-	3.20	114	46.700	5.240	2.300	345	52.00	-
11	10/29/81	91	-	3.10	114	49.500	5.900	2.420	365	62.62	-
12	11/5/81	98	-	3.10	120	49.700	5.310	2.260	360	45.39	-
13	11/12/81	105	-	3.20	104	48.300	5.270	2.160	350	54.54	-
14	11/19/81	112	-	3.20	116	50.500	5.130	2.190	330	57.57	-
15	11/25/80	118	-	3.30	110	50.300	5.230	1.990	400	55.55	-
16	12/4/81	127	-	3.30	62	52.400	5.610	2.080	350	60.60	-
17	12/10/81	133	-	3.60	280	54.000	5.580	2.230	360	62.62	-
18	12/17/81	140	-	4.20	282	51.900	5.230	5.180	320	63.63	-
19	12/24/81	147	-	3.40	112	52.200	5.350	1.980	360	57.57	-
20	12/31/81	154	-	3.60	106	53.700	5.270	1.990	360	59.59	-
21	1/7/82	161	-	3.70	136	24.900	2.740	1.270	365	18.36	-
22	1/14/82	168	-	3.50	128	27.900	2.750	1.080	360	31.11	-
23	1/21/82	175	-	3.30	130	49.600	5.420	2.290	345	51.51	-
24	1/28/82	182	-	3.40	106	46.700	4.980	2.190	350	42.30	-
25	2/4/82	189	-	3.40	120	45.800	5.180	2.500	385	45.50	-
26	2/11/82	196	-	3.30	120	42.900	5.090	2.660	330	33.66	-
27	2/18/82	203	-	3.20	100	46.200	5.600	3.150	335	43.35	-
28	2/25/82	210	-	3.40	150	43.700	5.020	2.720	370	33.66	-
29	3/4/82	217	-	3.40	116	41.900	5.030	2.590	350	41.31	-
30	3/11/82	224	-	3.20	100	42.000	5.190	2.740	350	40.29	-
31	3/19/82	232	-	3.20	100	35.600	4.600	2.600	330	35.19	-
32	3/25/82	238	-	3.20	132	33.200	4.500	2.520	340	33.00	-
33	4/1/82	245	-	3.20	112	32.600	4.530	2.580	315	30.60	-
34	4/15/82	259	-	3.10	98	26.000	4.210	2.920	270	20.16	-
35	4/22/82	266	-	3.10	114	28.200	4.290	2.360	280	19.95	-
36	4/30/82	274	-	3.10	120	13.330	4.520	3.050	270	13.00	-
37	5/6/82	280	-	3.10	114	27.360	4.490	3.330	275	18.06	-
38	5/14/82	288	-	3.20	132	26.400	4.370	2.780	295	20.16	-
39	5/21/82	295	-	3.20	128	28.700	4.630	2.330	270	26.52	-

Appendix F

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO ₄	FE++	AL Load
40	5/26/82	300	-	3.20	104	8.900	4.760	3.100	310	3.41	-
41	6/4/82	309	-	3.20	100	36.500	4.770	2.580	320	27.00	-
42	6/10/82	315	-	3.10	118	31.200	4.980	3.290	325	20.58	-
43	6/18/82	323	-	3.10	118	26.200	4.390	2.880	305	16.59	-
44	6/24/82	329	-	3.10	122	26.400	4.590	3.190	305	18.69	-
45	7/1/82	33	-	3.20	118	24.900	4.350	3.160	375	20.37	-
46	7/8/82	343	-	3.10	124	28.300	4.540	-	315	24.48	-
47	7/14/82	349	-	3.20	130	28.800	4.830	3.520	295	28.40	-
48	7/22/82	357	-	3.20	120	30.400	4.630	3.300	300	-	-
49	7/29/82	364	-	3.20	112	35.900	4.680	2.890	296	30.60	-
50	8/5/82	371	-	3.20	104	39.100	4.890	3.080	305	35.70	-
51	8/12/82	378	-	3.20	122	45.600	5.440	2.670	316	43.35	-
52	8/19/82	385	-	3.20	90	35.900	4.920	2.540	320	35.70	-
53	8/26/82	392	-	3.20	106	10.000	5.420	2.470	315	8.67	-
54	9/2/82	399	-	3.20	122	40.700	5.460	2.360	315	39.90	-
55	9/9/82	406	-	3.20	100	34.400	4.750	2.280	345	31.00	-
56	9/16/82	413	-	3.20	112	42.900	4.890	2.420	325	42.00	-
57	9/23/82	420	-	3.20	120	50.700	5.410	1.850	315	43.35	-
58	10/7/82	434	-	3.20	128	47.700	5.290	2.230	365	46.41	-
59	10/14/82	441	-	3.30	124	58.900	4.880	2.200	375	53.00	-
60	10/21/82	448	-	3.40	-	61.900	5.090	2.320	335	55.00	-
61	10/28/82	455	-	3.20	118	57.000	5.240	2.060	315	55.00	-
62	11/4/82	462	-	3.50	120	60.200	5.380	1.910	320	55.00	-
63	11/12/82	470	-	3.30	120	59.500	5.780	1.020	345	56.00	-
64	11/19/82	477	-	3.20	128	22.400	5.970	1.900	345	60.00	-
65	11/26/82	484	-	3.50	130	56.600	5.650	2.120	345	60.00	-
66	12/3/82	491	-	3.10	116	54.300	4.730	2.200	345	54.00	-
67	12/10/82	498	-	3.80	120	48.800	5.580	1.940	345	48.00	-
68	12/17/82	505	-	3.50	110	63.500	5.830	2.030	335	57.00	-
69	12/23/82	511	-	3.20	126	59.100	5.640	2.250	345	50.00	-
70	12/28/82	516	-	3.20	122	54.500	5.490	2.280	345	50.00	-
71	1/6/83	525	-	3.30	254	55.900	5.270	2.030	335	47.00	-
72	1/13/83	532	-	3.30	118	53.960	5.230	1.990	315	50.00	-
73	1/20/83	539	-	3.30	148	53.600	5.320	2.220	290	39.00	-
74	1/27/83	546	-	3.20	120	55.100	5.160	2.250	325	49.00	-
75	2/3/83	553	-	3.40	136	52.000	5.390	2.140	310	50.00	-
76	2/10/83	560	-	3.30	120	32.400	4.810	2.580	360	30.00	-
77	2/17/83	567	-	3.10	106	31.900	4.730	2.730	275	30.00	-
78	2/24/83	574	-	3.20	110	31.500	4.630	2.770	255	31.00	-
79	3/3/83	581	-	3.10	120	30.800	4.810	0.770	305	30.00	-

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO ₄	FE++	AL Load
80	3/10/83	588	-	3.20	120	36.900	4.980	3.190	155	35.00	-
81	3/17/83	595	-	3.10	110	33.800	4.860	2.820	300	33.00	-
82	3/25/83	603	-	3.30	102	32.300	5.000	2.460	280	28.00	-
83	3/31/83	609	-	3.30	100	30.400	4.840	2.700	225	21.00	-
84	4/7/83	616	-	3.30	106	23.600	4.240	3.470	265	19.00	-
85	4/14/83	623	-	3.10	136	23.600	5.130	3.260	280	12.00	-
86	4/21/83	630	-	3.10	104	19.000	6.870	4.040	305	6.63	-
87	4/28/83	637	-	3.10	112	19.000	6.920	3.480	295	-	-
88	5/5/83	644	-	3.10	128	19.400	7.630	3.440	355	8.40	-
89	5/12/83	651	-	3.10	120	19.000	7.480	-	357	6.63	-
90	5/19/83	658	-	3.10	112	16.700	6.530	3.670	345	6.63	-
91	5/26/83	665	-	4.40	134	5.700	5.200	-	420	5.10	-
92	6/2/83	672	-	3.10	136	17.400	6.400	3.120	285	8.80	-
93	6/9/83	679	-	3.00	115	19.600	6.500	3.260	325	8.67	-
94	6/16/83	686	-	3.10	114	18.400	5.820	2.950	275	11.22	-
95	6/23/83	693	-	3.10	210	17.200	6.110	4.180	365	15.81	-
96	6/30/83	700	-	3.10	342	23.800	5.710	2.310	335	21.42	-
97	7/7/83	707	-	3.10	116	12.900	5.000	3.500	295	12.00	-
98	7/14/83	714	-	3.10	108	15.020	5.630	2.770	300	15.00	-
99	7/20/83	720	-	3.10	116	27.700	5.350	2.880	285	27.70	-
100	7/28/83	728	-	3.10	154	28.900	5.300	2.240	321	28.80	-
101	8/4/83	735	-	3.20	96	6.100	5.750	2.100	299	6.00	-
102	8/18/83	749	-	3.10	98	21.900	5.190	2.280	265	21.90	-
103	8/25/83	756	-	3.10	116	31.700	5.150	2.350	510	31.70	-
104	9/8/83	770	-	3.10	172	35.300	5.600	2.290	260	35.30	-
105	9/15/83	777	-	3.10	108	37.100	5.700	1.970	285	37.00	-
106	9/22/83	784	-	3.20	156	38.000	5.900	2.040	340	38.00	-
107	9/29/83	791	-	3.10	198	18.200	5.920	1.680	310	-	-
108	10/6/83	798	-	3.10	176	39.900	6.020	1.270	320	-	-
109	10/13/83	805	-	3.10	180	34.400	5.510	1.840	275	-	-
110	10/20/83	812	-	3.20	170	34.960	5.210	2.140	320	34.90	-
111	10/27/83	819	-	3.20	158	40.900	5.850	1.750	355	408.00	-
112	11/3/83	826	-	3.20	124	38.400	5.510	1.640	330	38.00	-
113	11/10/83	833	-	3.20	176	38.200	5.540	1.800	300	38.10	-
114	11/17/83	840	-	3.20	134	40.900	5.950	1.930	362	40.00	-
115	11/23/83	846	-	3.10	134	42.370	5.930	2.010	334	41.00	-
116	12/1/83	854	-	3.20	102	34.580	5.240	2.110	295	-	-
117	12/8/83	861	-	3.20	114	29.640	5.170	1.980	285	14.49	-
118	12/14/83	867	-	3.20	104	27.900	4.310	2.510	295	27.50	-
119	12/22/83	875	-	3.30	114	21.090	5.050	3.970	260	14.91	-
120	12/29/83	882	-	3.40	108	17.350	4.730	2.700	225	14.49	-

Appendix F

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO ₄	FE++	AL Load
121	1/5/84	889	-	3.20	110	18.310	5.010	4.240	283	16.38	-
122	1/12/84	896	-	3.20	150	13.650	3.430	1.910	350	12.60	-
123	1/19/84	903	-	3.30	54	11.390	2.620	1.280	158	-	-
124	1/26/84	910	-	3.00	142	26.300	4.940	2.730	292	25.50	-
125	2/2/84	917	-	3.10	106	25.650	5.150	1.800	283	-	-
126	2/9/84	924	-	3.10	120	28.000	5.290	2.330	292	27.50	-
127	2/16/84	931	-	3.10	112	22.220	4.660	2.070	258	18.80	-
128	2/23/84	938	-	3.20	122	3.810	5.420	2.460	316	3.80	-
129	3/1/84	945	-	3.20	154	18.770	5.340	3.440	269	10.20	-
130	3/8/84	952	-	3.30	194	16.840	5.180	2.730	341	12.81	-
131	3/15/84	959	-	3.20	184	19.190	5.570	3.220	307	18.69	-
132	3/22/84	966	-	3.20	218	24.860	5.780	2.960	316	24.50	-
133	3/30/84	974	-	3.20	110	23.540	5.110	2.500	291	23.50	-
134	4/5/84	980	-	3.20	114	25.300	5.090	2.760	291	0.66	-
135	4/13/84	988	-	3.20	108	14.650	5.180	1.700	272	11.55	-
136	4/19/84	994	-	3.20	94	14.430	5.310	2.050	264	10.71	-
137	5/3/84	1008	-	3.20	152	13.500	4.900	2.700	260	10.71	-
138	5/10/84	1015	-	3.20	80	16.400	5.300	2.100	286	9.45	-
139	5/17/84	1022	-	3.20	144	12.800	4.900	2.300	235	8.19	-
140	5/24/84	1029	-	3.20	156	12.300	4.700	1.500	272	6.09	-
141	6/7/84	1043	-	3.10	172	11.000	3.900	2.200	272	8.80	-
142	6/21/84	1057	-	3.20	184	6.800	3.800	2.200	264	6.00	-
143	6/28/84	1064	-	3.10	144	16.370	5.180	1.870	243	9.34	-
144	7/12/84	1078	-	3.10	128	12.700	5.100	2.600	245	-	-
145	7/19/84	1085	-	3.10	110	12.300	3.700	2.500	277	9.87	-
146	7/26/84	1092	-	3.10	124	12.300	4.300	2.100	256	-	-
147	8/2/84	1099	1623	3.10	152	13.600	4.200	2.700	317	28.15	81.9
148	8/9/84	1106	1356	3.10	110	20.600	1.200	0.800	249	20.60	19.6
149	8/23/84	1120	1186	3.10	98	23.800	4.500	2.600	270	24.10	64.2
150	8/30/84	1127	1104	3.10	118	34.000	4.600	2.300	305	33.15	61.0
151	9/6/84	1134	1064	3.10	120	33.200	5.000	2.000	290	32.13	63.9
152	9/13/84	1141	1024	3.10	122	35.000	4.900	2.100	276	33.66	60.3
153	9/20/84	1148	1024	3.10	114	21.500	4.200	2.200	255	7.59	51.7
154	9/27/84	1155	984	3.10	118	24.200	4.200	2.300	275	24.20	49.7
155	10/4/84	1162	907	3.10	110	21.000	5.000	2.400	274	21.00	54.5
156	10/11/84	1169	869	3.10	106	25.700	5.500	2.900	298	25.70	57.4
157	10/18/84	1176	831	3.10	110	27.800	5.500	2.600	255	27.80	54.9
158	10/25/84	1183	794	3.10	110	25.300	6.700	2.500	284	28.05	63.9
159	11/1/84	1190	794	3.20	110	6.900	4.900	3.500	282	6.90	46.8
160	11/8/84	1197	794	3.20	114	25.100	6.600	3.500	293	25.10	63.0

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO₄	FE++	AL Load
161	11/15/84	1204	794	3.20	126	27.000	5.100	4.000	285	27.00	48.7
162	11/21/84	1210	757	3.20	120	44.000	5.200	1.900	320	44.00	47.3
163	11/29/84	1218	1186	3.20	102	30.000	5.700	2.800	310	47.40	82.4
164	12/6/84	1225	1443	3.30	106	30.000	5.090	2.220	261	45.00	88.3
165	12/13/84	1232	1356	3.20	118	29.569	4.424	1.756	265	29.50	72.1
166	12/20/84	1239	1270	3.20	124	31.290	4.834	1.940	291	31.29	73.8
167	12/28/84	1247	1399	3.20	106	33.961	5.166	1.867	287	33.96	86.9
168	1/3/85	1253	1443	3.20	102	32.794	4.894	2.209	263	32.75	84.9
169	1/10/85	1260	1399	3.30	118	23.094	3.798	1.126	253	33.09	63.9
170	1/17/85	1267	1313	3.40	92	12.510	2.068	0.751	271	12.51	32.6
171	1/24/85	1274	1186	3.50	108	26.331	4.319	1.709	249	26.33	61.6
172	1/31/85	1281	1186	3.30	102	21.965	3.439	1.459	273	20.90	49.0
173	2/7/85	1288	1104	3.40	104	32.125	4.490	2.266	270	27.50	59.6
174	2/14/85	1295	1762	3.30	110	27.006	3.766	0.943	274	27.01	79.8
175	2/21/85	1305	1715	3.20	100	47.837	4.587	1.968	261	21.40	94.6
176	2/28/85	1309	1904	3.20	90	27.706	4.496	2.264	237	17.34	102.9
177	3/7/85	1316	1608	3.20	96	24.718	4.062	2.120	240	15.54	78.5
178	3/14/85	1323	1399	3.20	88	25.887	4.299	1.963	238	16.17	72.3
179	3/21/85	1330	1313	3.20	90	29.120	4.684	2.077	219	19.53	73.9
180	3/28/85	1337	1228	3.20	98	20.675	3.824	1.778	247	18.90	56.4
181	4/4/85	1344	1313	3.20	100	25.545	4.462	2.678	252	20.91	70.4
182	4/11/85	1351	1443	3.20	100	26.890	4.587	1.925	259	20.40	79.6
183	4/18/85	1358	1443	3.10	92	23.168	4.023	1.489	253	4.93	69.8
184	4/25/85	1365	1356	3.20	96	25.092	4.331	1.795	253	15.30	70.6
185	5/2/85	1372	1270	3.20	104	25.374	4.309	1.511	252	20.91	65.8
186	5/9/85	1379	1577	3.10	96	29.277	4.715	2.276	236	23.46	89.4
187	5/16/85	1386	1488	3.10	80	28.376	4.154	2.400	246	19.89	74.3
188	5/23/85	1393	1399	3.10	92	25.557	3.637	0.954	227	23.00	61.2
189	5/30/85	1400	1270	3.10	92	20.992	3.478	1.399	246	17.20	53.1
190	6/6/85	1407	1186	3.10	86	22.321	3.622	1.399	247	15.50	51.6
191	6/13/85	1414	1145	3.20	90	28.997	3.551	1.509	237	23.50	48.9
192	6/20/85	1421	1145	3.20	92	29.512	2.815	1.079	261	28.56	38.7
193	6/27/85	1428	1104	3.30	100	33.395	4.877	1.606	266	30.60	64.7
194	7/3/85	1434	1064	3.30	80	32.667	4.807	1.499	257	29.58	61.5
195	7/11/85	1442	1024	3.30	128	49.871	7.465	1.663	281	28.05	91.9
196	7/18/85	1449	984	3.20	86	33.180	4.661	1.591	300	33.15	55.1
197	7/25/85	1456	907	3.30	78	33.349	4.754	1.632	284	33.00	51.8
198	8/1/85	1463	907	3.30	92	35.080	4.948	1.668	270	34.00	53.9
199	8/8/85	1470	869	3.20	98	29.991	4.153	1.333	285	34.50	43.4
200	8/15/85	1477	869	3.30	92	41.140	4.445	1.418	254	35.50	46.4

Appendix F

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO ₄	FE++	AL Load
201	8/22/85	1484	831	3.40	110	36.620	5.055	1.178	229	36.00	50.5
202	8/29/85	1491	794	3.30	106	35.917	4.762	1.443	274	35.50	45.4
203	9/5/85	1498	794	3.20	90	39.801	5.061	1.290	270	36.00	48.3
204	9/12/85	1505	794	3.30	134	32.232	4.418	0.922	271	32.00	42.2
205	9/19/85	1512	794	3.40	106	42.605	5.041	1.274	279	39.50	48.1
206	9/26/85	1519	794	3.40	118	41.471	5.469	1.199	292	37.00	52.2
207	10/3/85	1526	869	3.40	114	40.882	5.219	1.500	309	39.00	54.5
208	10/10/85	1533	869	3.30	94	44.588	5.775	1.889	283	39.00	60.3
209	10/17/85	1540	831	3.30	102	36.542	5.115	1.284	298	38.00	51.1
210	10/24/85	1547	831	3.30	102	38.551	4.698	1.340	299	36.00	46.9
211	10/31/85	1554	794	3.30	96	39.511	5.322	1.608	313	38.00	50.8
212	11/7/85	1561	794	3.20	86	37.989	4.781	1.009	294	38.00	45.6
213	11/14/85	1568	794	3.20	90	42.059	5.533	1.301	293	39.50	52.8
214	11/22/85	1576	907	3.20	82	40.527	5.078	1.587	325	20.50	55.4
215	11/27/85	1581	1024	3.20	96	49.232	6.378	2.421	320	38.50	78.5
216	12/5/85	1589	1809	3.30	90	33.762	4.554	1.596	285	33.50	99.0
217	12/12/85	1596	1715	3.30	114	27.262	4.384	2.063	281	27.00	90.4
218	12/19/85	1603	1577	3.20	92	25.320	4.607	2.167	263	25.00	87.3
219	12/26/85	1610	1399	3.20	88	28.270	5.294	2.043	306	25.00	89.0
220	1/2/86	1617	1228	3.30	94	27.100	5.885	3.337	296	27.00	86.9
221	1/9/86	1624	1145	3.30	96	33.434	5.712	2.410	291	28.50	78.6
222	1/16/86	1631	1104	3.30	108	33.000	4.050	0.800	325	29.50	53.7
223	1/23/86	1638	1104	3.20	104	34.800	5.260	2.138	330	31.50	69.8
224	1/30/86	1645	1270	3.30	128	39.300	5.410	2.014	293	37.50	82.6
225	2/6/86	1652	1313	3.30	92	35.500	5.036	2.410	302	34.50	79.5
226	2/13/86	1659	1488	3.20	100	39.000	5.260	2.390	297	33.00	94.1
227	2/20/86	1666	2298	3.20	104	33.500	5.120	2.085	287	31.00	141.4
228	2/27/86	1673	4793	3.30	130	22.900	8.160	5.870	326	13.50	470.1
229	3/6/86	1680	2767	3.20	92	19.700	6.230	3.890	331	15.20	207.2
230	3/13/86	1687	2767	3.20	114	19.400	5.470	3.320	348	16.00	181.9
231	3/20/86	1694	6533	3.30	106	11.100	5.180	3.804	282	4.00	406.8
232	3/27/86	1701	3772	3.30	78	11.800	5.170	3.240	281	5.70	234.4
233	4/3/86	1708	2820	3.30	98	11.300	3.950	2.420	259	10.00	133.9
234	4/10/86	1715	2198	3.40	94	16.400	5.065	2.930	254	12.30	133.8
235	4/17/86	1722	2820	3.30	98	18.300	5.240	2.501	252	13.00	177.6
236	4/24/86	1729	4547	3.40	80	11.200	4.970	2.850	244	4.50	271.6
237	5/1/86	1736	3371	3.40	82	10.300	4.460	2.680	250	5.83	180.7
238	5/8/86	1743	2555	3.40	82	13.700	5.104	2.770	255	3.70	156.7
239	5/15/86	1750	2000	3.30	98	21.200	5.530	3.360	210	3.30	132.9
240	5/22/86	1757	4006	3.40	114	16.400	5.170	2.480	259	12.20	248.9

Statistical Analysis of Abandoned Mine Drainage in the Assessment of Pollution Load

ROW	DATE	DAYS	Flow	pH	Acidity	FE	MN	AL	SO₄	FE++	AL Load
241	5/29/86	1764	3427	3.40	32	11.800	4.980	3.000	257	5.00	205.1
242	6/5/86	1771	2608	3.30	76	18.700	5.040	2.480	257	8.40	158.0
243	6/12/86	1778	2049	3.40	102	16.300	5.370	2.560	246	12.00	132.3
244	6/19/86	1785	1762	3.40	86	17.100	5.640	2.570	247	12.40	119.5
245	6/26/86	1792	1532	3.30	94	14.100	5.310	2.630	222	13.00	97.8
246	7/2/86	1798	1399	3.30	102	20.200	7.280	2.520	243	14.91	122.4
247	7/10/86	1806	1270	3.30	100	22.900	5.610	2.470	256	18.50	85.6
248	7/17/86	1813	1186	3.30	100	24.900	6.860	2.230	254	19.00	97.8
249	7/24/86	1820	1145	3.30	92	22.200	5.060	2.070	254	20.00	69.6
250	8/1/86	1828	1270	3.20	102	20.100	4.930	1.990	271	20.10	75.3
251	8/7/86	1834	1228	3.20	86	25.100	5.820	2.180	252	20.50	85.9
252	8/14/86	1841	1145	3.30	86	24.100	5.310	2.150	280	19.00	73.1
253	8/21/86	1848	1064	3.20	94	26.300	5.690	2.300	293	21.50	72.8
		max	6533	4.40	342	63.500	8.160	5.870	510	408.00	470.1
		min	757	3.00	30	3.810	1.200	0.751	155	0.66	0.0
		Avg	1504	3.24	117	30.703	5.044	2.322	298	29.66	38.0
		Med	1228	3.20	110	28.997	5.100	2.265	293	27.70	0.0

