T-4397

PREDICTION OF ZINC AND IRON LOADS IN THE COLORADO UPPER ARKANSAS RIVER BASIN USING MULTIPLE LINEAR REGRESSION

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Mathematical and Computer Sciences).

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ABSTRACT

Mining for precious metals in the Leadville area near the Arkansas River has caused contamination of the waterways. Several sites in the area have been monitored to quantify the amounts of heavy metal contamination. Obtaining the heavy metal loads by lab analysis is a long, expensive process. Knowledge of heavy metal loads in the streams without taking the actual measurement of the metals is beneficial to the assessment of the water quality in the upper Arkansas River.

Multiple linear regression techniques were used to provide predictive models for the estimation of zinc and iron loads in the upper Arkansas. Data was obtained from two sites over a period of two years. One site lies directly below a mine drainage site. After the first year of data collection, a water treatment plant (Leadville Drain treatment plant) was installed just above this site. The second site is on the main stem of the Arkansas and also shows the effects of water treatment. Models were built for each site, year, and metal load.

Several environmental factors affect the presence of heavy metal loads in streams. Much of the variability in

the occurrence of the metal loads was accounted for in the models. The results were surprisingly good considering the expected variations in field work. Variables used to predict iron and zinc loads included stream discharge, iron particulate, specific conductance, water temperature, pH, turbidity, and a seasonal variable -- cumulative days. Although several models have aspects in common, none are the same. This is expected as there is significant variability among site locations as well as before and after water treatment. Stream discharge and iron particulate proved to be important predictors for estimating the metal loads.

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ACKNOWLEDGMENTS

I would like to thank my thesis advisor, Professor Bill Astle, of Colorado School of Mines Mathematical and Computer Sciences Department, for his direct approach and the excellent guidance he provided in completing this study. He gave a great deal of his personal time and energy to ensure schedules were met. I also thank Dr. Katherine Walton-Day, my project manager of the U. S. Geological Survey Water Resource Division, for providing me with this interesting project. Her knowledge of water chemistry and general support were critical to the success of this study. Finally, my gratitude goes to Frank Liptak, my husband, who sacrificed so much of his time to care and provide for our family while I completed this thesis.

Chapter 1
BACKGROUND

Water flowing from the Rocky Mountain Region is a valuable resource to many communities. Not only do local cities such as Denver depend on the water flow, but so do other large metropolises like Phoenix and Los Angeles.

The three major threats to mountain water quality (in order of severity) are mining (past and present), acid rain (or acid snow), and industrial waste (NOVA 1990). From a water quality viewpoint, the Colorado Rocky Mountain waterways are among the most endangered in the Western states (NOVA 1990).

The discoveries of gold, silver, lead, and zinc in the Rocky Mountains about the year 1858 began a mining boom. Most of the land in the West was public and was mined freely with no regulations. Leadville Colorado is the area considered as having the nations most contaminated waters due to mining (NOVA 1990). Leadville has more than a 100 year "legacy of unregulated mining" (NOVA 1990).

There were three types of mining operations that were popular during the gold and silver mining days. Miners used either high pressure hoses to loosen the ore from the mountain or dredging techniques. The third and most detrimental method to the waterways (long term) was hard rock mining that dug tunnels into the mountain and leached the ore with the use of acidic solutions (NOVA 1990).

Acid mine drainage is formed by the exposure of the bedrock in the walls of underground mines to aquifers (underground water systems). Water from the aquifers comes up through the mine shafts and leaches many trace elements along the way then becoming surface water (NOVA 1990). The oxidation and acid dissolution of pyrite (an iron sulfide) in the bedrock causes high concentrations of sulfate and trace metals such as iron, zinc, aluminum, lead, copper, arsenic, nickel, mercury, cadmium, silver and manganese to be released to the ecosystem (USDA -- United States Department of Agriculture 1993).

Acid water is still draining out of mine sites in Leadville causing a continuous flow of contamination to streams and ultimately to the Arkansas River. There may not be an end to the flow coming from the Leadville mine sites as an unlimited supply of water seems to be available from the aquifer. This poses a serious health risk to the area. As of January 1990, there were three million gallons of acid mine drainage coming out of two sites in Leadville (the YAK Tunnel and the Leadville Drain) (NOVA 1990). This equates to one ton of heavy metals flowing into the streams per day.

This rate has had very little fluctuation over the past thirty years (NOVA 1990).

The low pH of the mine drainage is one factor that causes heavy metals to pose a problem to the environment. The lower the pH, the easier it becomes for some metals (such as copper, lead, and zinc) to be leached downstream and spread into the ecosystem. The USDA estimates 5,000 to 10,000 miles of streams are seriously affected in the United States (USDA 1993). In 1988, the Colorado Health Department stated 1,300 miles of streams in the Colorado Rockies have been damaged due to mining (NOVA 1990). The United States Fish and Wildlife Service (USFWS) estimates 64 miles of the upper Arkansas river basin are impacted by heavy metals (USFWS 1993).

Billions of tons of tailings left behind is another problem due to the mining process. Tailings are fine granules left over from mining the ore. Extraction from the ore left significant amounts of heavy metals in the tailings. This was not only due to the inefficient techniques of the times but also due to lack of concern for many of the less valuable heavy metals that were later discovered to be dangerous. The remnants were often dumped along side streams or in stream beds where more contamination could begin. Most of these tailing piles still remain, and some continue to damage surrounding ecosystems (NOVA 1990), depending on their contents.

Some of the toxic metals found in the waters below Leadville are iron, zinc, and lead. Other potentially hazardous metals also have been detected such as cadmium and selenium. Each of these metals poses a potential health risk.

Usually, iron alone in the waterways would not pose a serious threat to health or the environment, although it is visually distasteful as deposits of iron can color the stream bed from a yellow to brown-orange color. It is the combination of iron and other metals that can harm ecosystems (USFWS 1993). There are ecosystems along certain streams in the West coming from mine drainage sites that are considered to be dead or severely damaged due to these metals (USDA 1993). The mine tailings along the California Gulch (a tributary to the Arkansas river) contain a very high iron content causing iron to leach into the water way. Iron is a very critical contaminant found in large amounts in the upper Arkansas River.

Iron helps control the behavior of many heavy metals in natural waters. This is because the large surface area and surface charge of small particles of iron hydroxide attract copper, lead, zinc, and other metals (Horowitz 1991).

Copper and lead normally require either a very low or very high pH level in order to be freely dissolved and mobile in water. However, with iron available to transport these metals, pH levels in the normal range for water (5-8 pH) are adequate to transport these metals. Therefore, with iron present, these metals can potentially spread further downstream than in the absence of iron. Thus their effects are more widespread.

Zinc also poses a problem in the upper Arkansas River. Some aquatic life cannot tolerate even a small amount of dissolved zinc (0.047 mg/L) (EPA 1986). Yet, much more than that has been measured in many sections of the river basin. Zinc concentrations in the Arkansas river directly below the Leadville Drain (see figure 1) varied from a low of about 0.08 mg/L to over a maximum of 70 mg/L in water samples taken from sites AR05, AR65, LD10, and CG99 in years 1986 through 1989 (Wetherbee and Kimball, 1991). Zinc can also travel freely dissolved as well as in conjunction with iron.

Chapter 2
INTRODUCTION

The broad scope of this project is to contribute to the analysis of the water quality in the Arkansas River basin. The usual method of determining the chemical composition of the water is to take several water samples in many locations and to conduct an extensive laboratory analysis to determine the concentration of about 25 to 30 different constituents. The focus of this research is on the statistical analysis of heavy metal loads detected in the Leadville area of the Arkansas River.

Objective of Analysis

The objective here is to apply regression methods in order to predict load levels for certain heavy metals and perhaps develop a more efficient way to determine metal loads. The plan for predicting the iron and zinc loads is to use multiple regression techniques. The relationships examined are the metals (the response variables) with possible predictors being: stream discharge, pH, conductivity, temperature, iron particulate, time (i.e., seasonal patterns), and sulfate and bicarbonate concentrations. The desired result of the statistical analysis is to be able to predict the concentration (or load -- a more useful variable) of the metal, without the time consuming and expensive procedure of a complete lab analysis.

Data Collection

The data provided by USGS was collected with the intention of executing the previously described study. The data comes from two sites along the upper Arkansas River. One site is on a tributary about one mile below the Leadville Drain treatment plant (built in January of 1991). This site will be referred to as site EF35.

Another treatment plant, the YAK Tunnel treatment plant, was built at the same time. Its effects may be shown in the analysis of the second site. The other site is on the Arkansas river near Malta just below Empire Gulch (to be referred to as AR65)(see figure 1). Samples were collected weekly from about April through October for the years 1991 and 1992. Lab analysis determined the concentration of roughly twenty-five different constituents in each sample. The data relevant to this study are found in the appendices.

The two sampling sites used were United States Geological Survey (USGS) gauging sites (mini-monitors) that were equipped to record stream stage (stream level), pH, temperature, and specific conductance every 30 minutes. This data is then transmitted via satellite to USGS databases. The stream stage record is converted to a stream discharge (flow) record using multiple measurements of stage and discharge along with standard USGS data reduction techniques as described in Measurement and Computation of Streamflow: Volume 1 Measurement of Stage and Discharge *and* Volume 2 Computation of Discharge (Rantz and others 1982).

There are difficulties in obtaining accurate data from a mini-monitor due to required maintenance of the mini-monitors. They often need cleaning and re-calibrating and may be sending poor data for several days before this is done. The data (water temperature, pH, and specific conductance) taken for this study were not obtained through a mini-monitor but were obtained at the time of water sampling by USGS employees who traveled to the sites. Precision equipment was used that was kept clean and calibrated between measurements. It was hoped that the type of data that can be obtained from a mini-monitor would be sufficient for predicting the metal loads. This would be a very inexpensive and easy way to determine metal loads as there are already several mini-monitors situated by USGS and the Environmental Protection Agency (EPA) in many mine drainage areas. Since this analysis is specific to the sites where data was obtained, similar analyses could be done at other sites to check for relationships of mini-monitor data with metal loads.

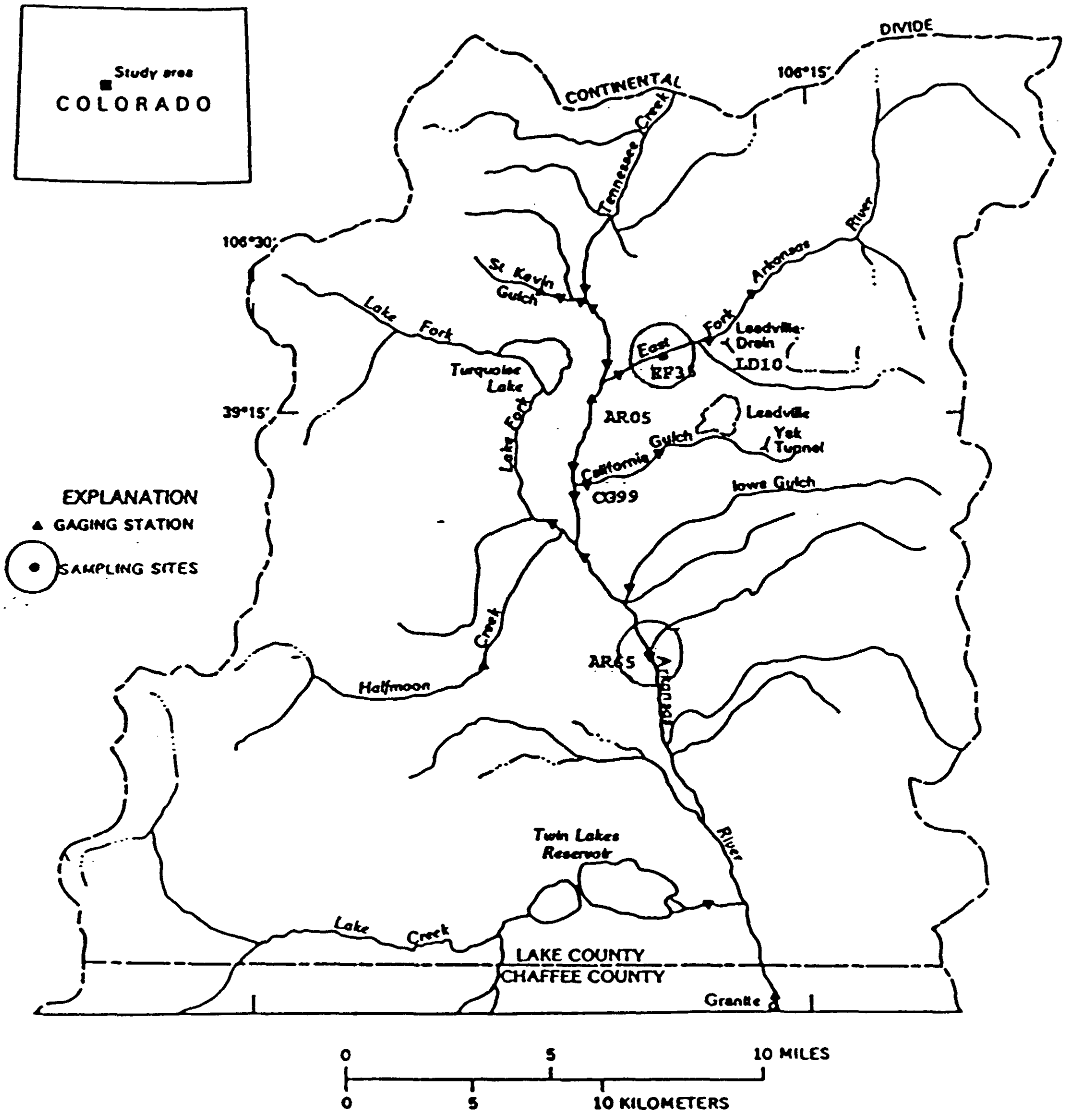

Figure 1. Map of study area. (Modified from Kimball 1987, fig. C-1)

Comparisons of the transmitted mini-monitor data and the manually recorded data of the gauging sites was done to determine how well the two recording methods agreed. In general, the values were very close for the sites studied. Therefore, mini-monitor data may be used in place of field data in this statistical study, provided the parameters given by mini-monitors are useful in metal prediction.

Once the concentration of the constituent (heavy metal in this instance) is determined, the metal load is calculated by taking the product of the concentration, the stream discharge (flow), and the appropriate constant for adjustment of the units. Note the following formula:

$$Load_i = Q_i * C_i * K \qquad (2.1)$$

where:

i is any single measurement,

Load is the metal load calculated in kg/day,

Q is the stream discharge in ft^3/second,

C is the constituent concentration in mg/l, and

K is 2.447 -- a constant to adjust units from (ft^3/sec) * (mg/L) to the load unit of Kg/day.

The sampling technique that was used is called a flow-weighted, depth and width integrated sample. This provides for a sample that is accurately representative of the river. Samples are collected by lowering and raising a hand-held sampler at an even rate at 10 to 20 locations spaced evenly across the width of the stream. The hand-held sampler contains two bottles that gradually fill with water as the sample is collected. Water from the two bottles is combined to represent the entire sample, and separate bottles of water are collected from this sample for analysis.

This integrated sampling technique is very important because a contaminant coming into the Arkansas from a tributary (California Gulch, for example) will remain on the side of the river it came in on for a very long distance. A lot of turbulence is required before the river becomes homogenous.

Nitric acid, a preservative, is added to the bottled samples that will be analyzed for heavy metals in order to avoid the aggregation of constituents in the water. Without the preservative, certain substances will precipitate in a very short amount of time and alter the results of the heavy metal tests. Nitric acid will not alter the results if used correctly. Control experiments are done to ensure the nitric acid is pure and cannot alter the samples. The technique for iron and zinc analysis is the Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) method. For a detailed report on this method, see Garbarino and Taylor 1985.

Chapter 3

METHODOLOGY OF MODEL DEVELOPMENT

The effort of this analysis begins by searching for a relationship between heavy metals in the stream and one or more other variables. Once a strong relationship is discovered, the variables may be used as predictors to calculate the quantity of the heavy metal. This prediction is based on techniques of regression. For example, it is desirable to be able to predict the zinc load at a certain location in the Arkansas River by knowing other information about the site such as the stream discharge (flow) or conductivity.

Linear Regression Technique

The simple linear regression equation for a full model is:

$$\mathbf{Y}_i = \beta_0 + \beta_1\mathbf{X}_i + \varepsilon_i \tag{3.1}$$

where:

$\mathbf{Y}_i$ is the value of the response variable in the i^{th} case,

X_i is the value of the predictor variable in the i^{th} case,

β_0 and β_1 are parameters to be estimated in the regression, and

ε_i is a random error term with a mean of zero and a variance, σ^2.

In the case of having more than one predictor in the model, additional terms are included in equation 3.1. For example, for two predictors, the equation is:

$$Y_i = \beta_0 + \beta_1 X_{1i} + \beta_2 X_{2i} + \varepsilon_i$$

where:

β_2 is another parameter to be estimated in the regression, and

X_{2i} is the value of the second predictor in the i^{th} case.

The relationship between the predictors and the metal load is statistical. It will not be perfect but will have some variation. This variation, σ^2, comes from the last term shown in equation 3.1. An analysis of this variation is done to determine the appropriateness of the model that is developed to represent the relationship.

The variance, σ^2, is equal to the expected value of the error mean square (MSE). MSE is determined by the following formulas:

$$MSE = \frac{SSE}{n-p} = \Sigma\frac{(Y_i-\hat{Y}_i)^2}{n-p} \tag{3.2}$$

where:

SSE is the error sum of squares -- the squared differences of the observed response (Y_i) and the estimated response($\hat{Y}_i$),

n is the number of data points in sample, and

p is the number of parameters to be estimated.

The lower the MSE value, the less variance in the model and the better the regression relation. This is one of the ways that the usefulness of the models is measured. The MSE values are displayed for all models in the analysis of variance tables in chapter 6, REGRESSION RESULTS.

Another way that adequacy of the model is determined is by the coefficient of determination (R^2; read as R-squared). The R^2 value describes the proportionate reduction in the total variation when using the predictor variables in the model to obtain the value of the response (dependent) variable. The mathematical equation for R^2 is determined by the formulas

$$R^2 = \frac{SSR}{SSTO} = 1 - \frac{SSE}{SSTO} \tag{3.3}$$

where:

SSTO (total sum of squares) is the measure of total variation in the model,

SSR (regression sum of squares) is the measure of variation between the regression line and the actual, observed value, and

SSE (error sum of squares) is the measure of variation for the residuals. Residuals are the difference between the observed value for the dependent variable and the predicted value provided by the model.

A precise definition of the above sums of squares can be found in many statistical texts (for example, Neter and others 1990). The values of these parameters can be found in the analysis of variance tables for each model developed. An R^2 value of 1.00 indicates a perfect relationship between the predictors and the metal load, whereas, an R^2 value near 0.00 indicates "a very poor fit".

An adjusted R-squared (R_a^2) value is also determined which gives a quick way to judge if the model is including variables that do not significantly contribute to the fit. The adjusted coefficient of multiple determination is defined as:

$$R_a^2 = 1 - \frac{(n-1)\,SSE}{(n-p)\,SSTO} \tag{3.4}$$

where:

SSE (error sum of squares) is the measure of variation for the residuals,

SSTO (total sum of squares) is the measure of total variation in the model,

n is the number of data points in sample, and

p is the number of parameters to be estimated.

The adjusted R-squared (R_a^2) value will be fairly close to the R-squared (R^2) value if the additional variables contribute more to the regression rather than the error. If the R_a^2 is much lower than the R^2, then the penalty for the additional variable out-weighs the benefit of the added accuracy. The R_a^2 is displayed with the regression results.

Examination of the residuals was also used to select the most appropriate model. Residuals are the difference between the observed value for the dependent variable and the predicted value provided by the model.

For the regression model obtained, there are two assumptions that must hold: error, ε_i, have a constant variance (homoscedasticity), and errors are normally distributed with zero mean.

The first assumption is tested by examining a plot of the residuals against their predicted values and against the predictor variables, the X_i's. If there is no apparent pattern in the residuals (such as a detectable expansion, sloping, or curvature over the predicted values) then there is no evidence of heteroscedasticity in the model.

The second assumption (normal distribution of the data) is tested by examining the probability plot within normality for the residuals. A normal probability plot is a plot of the sorted residuals against the corresponding values of a mathematical normal distribution (the expected value if the data follows a normal distribution). This plot can be used to screen data for outliers or to examine residuals for non normality. As an example, a probability plot for iron load from site AR65 in 1992 is shown in figure 2.

If the data are normally distributed, then the plotted values should lie approximately on a straight line. Many of the normal probability plots have slight curvatures at the extremities which indicates that the tails are shorter or longer, depending on the direction of curvature, than what is expected from a normal distribution. This slight difference does not invalidate the model. In figure 2, the probability plot shows a slight downward curvature indicating the need for a transformation on the variable.

This is discussed in more detail in chapter 5, MODEL BUILDING.

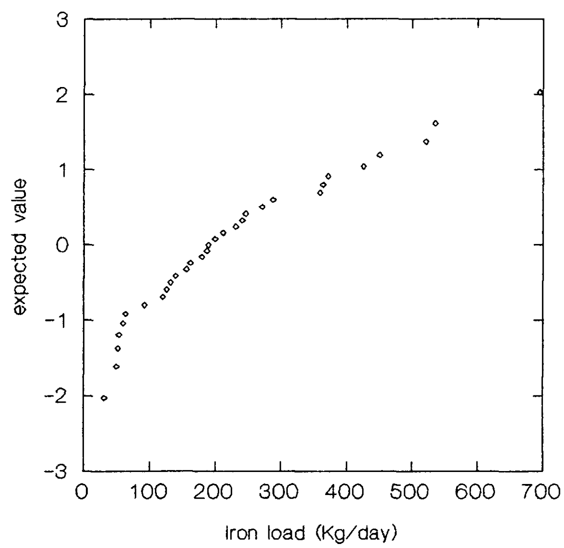

Figure 2. Probability plot for iron load at site AR65 in 1992.

The residuals of the models were also used to examine if other variables should be included in the model. Plots of residuals versus the other variables indicate whether that variable had an important effect on the dependent variable.

Residuals were also plotted against the included independent variables to determine the appropriateness of the magnitude of the independent variable. For example, if a curved effect is observed in the plot, then the power of the independent variable needs adjusting.

The development of the regression models using ordinary least-squares regression was with the aid of a statistical package: SYSTAT for Windows, Version 5. A forward stepwise regression algorithm was employed for each data set to find the "best" subset of independent variables for each model. This technique is based on the use of the F^* statistic. The general F^* statistic is obtained by the formula:

$$F^* = \frac{MSR}{MSE} \tag{3.5}$$

where MSR and MSE are the regression mean square and error mean square, respectively. MSR is SSR divided by its associated degrees of freedom. A more detailed analysis of the regression results is found in chapter 6, REGRESSION RESULTS.

Selection of Response Variables

Since iron is such a critical metal in this instance, discussion will begin by concentrating on this metal. The second metal to analyze will be zinc.

The response (dependent) variables of most concern to this analysis are iron (Fe) loads and zinc (Zn) loads. This is due to the potential health or environment hazard that these heavy metals can cause. Data was also available for calcium (Ca), magnesium (Mg), and sodium (Na). Calcium exists naturally and abundantly in the rivers and streams. A plot of calcium concentration in 1991 and 1992 is included as an example of a metal unaffected by water treatment. There is no set maximum level for either human consumption or aquatic life for calcium or magnesium (EPA 1986). Sodium (Na) is being used in the treatment of the mine drainage just above one of the sites analyzed. The treatment allows some of the more hazardous metals to precipitate out of the water. This leads to an increase in the amount of sodium detected below the Leadville Drain treatment plant.

The drinking standard for iron (Fe) is 0.300 mg/L (EPA 1986) and was frequently being surpassed (0.8 mg/L at site EF35 and 2 mg/L at site AR65) in 1991 (before treatment) (see figures 3b and 4b in chapter 4, PRELIMINARY ANALYSIS). A yearly comparison of the data showed a significant reduction in iron concentration after treatment. Zinc concentrations were also reduced after treatment. Zinc was exceeding the standard of 0.047 mg/L for aquatic life (EPA 1986) before treatment (see figures 3a and 4a in chapter 4, PRELIMINARY ANALYSIS). Plots are shown in figures 6a through 6d showing the difference of metal concentration from 1991 (before water treatment) and 1992 (after water treatment).

Selection of Predictor Variables

In the regression analysis, the metal load was the dependent variable (to be predicted) and the independent variables (predictors) were usually stream discharge, iron particulate, temperature, and/or a time (seasonal) variable. Other possible predictors considered were specific conductance, pH values of the water, bicarbonate concentrations, and sulfate concentrations. Specific conductance was thought to be a likely predictor as it is a measure of electrical conductivity which would generally increase in the presence of heavy metals. However, there is a high correlation between specific conductance and stream discharge, and stream discharge almost always proved to be a stronger predictor. Since the acidity of the water contributes to the leaching of heavy metals, it seemed likely for pH to be in the model. Heavy metal loads were not often predicted using pH probably due to the fact that the pH readings of the water stayed within a fairly narrow range yet the heavy metal loads usually fluctuated widely. Using the same logic with temperature, this is why temperature did not show a strong relationship (although it was significant enough to be included in some models). The bicarbonate and sulfate concentrations were available for the analysis as experimental variables but did not show an adequate correlation to be part of the final model.

Iron particulate cannot be obtained as easily as the other predictors. Iron particulate concentration was calculated the following way:

Iron particulate = [FeT] - [FeD]

where:

[FeT] = total measured iron concentration

[FeD] = dissolved iron concentration.

Total iron concentration is measured from an unfiltered sample. The dissolved iron concentration was measured after filtering the sample through a 0.10-μm (micrometer) filter.

The other predictors discussed can be obtained almost instantly from several sites via a mini-monitor that can send data through satellite transmissions.

Unfortunately, iron particulate cannot be obtained from a mini-monitor. The regression models often rely on the knowledge of iron particulate to predict both iron and zinc, therefore, for the accuracy that has been obtained in the models, the mini-monitor data by itself is usually insufficient. A sometimes less accurate model is also provided for the instance of only having the mini-monitor data to use when the model is satisfactory.

Another possible predictor is turbidity. It was hoped that turbidity could be used to replace iron particulate. The data set for this report contains a turbidity measurement only for 1992 therefore a yearly comparison is impossible. Turbidity is a measurement of the cloudiness of the water. Since iron particulate can be a significant component in cloudy water, this may be a possible replacement predictor. This potentiality is examined in the analysis. If it proves to be productive, it is possible to modify the mini-monitors so that turbidity is measured continuously and readily available.

Chapter 4

PRELIMINARY ANALYSIS

Initial examination of the data show several dynamics occurring during the two years of data collection. Some of the major dynamics noted were: effects of the water treatment plants (the Leadville Drain and the YAK Tunnel), seasonal behavior of the constituents and predictor variables, stronger influences for site EF35 compared with site AR65 due to water treatment, and relationships between variables.

The first observation in studying the concentrations of the constituents is the apparent effect of the water treatment plant at the Leadville Drain. The Leadville Drain treatment plant was in operation in February of 1992. Water samples for this project were collected before and after installation. Thus, there is a six month gap between the 1991 and 1992 data sets.

Naturally, there were a few outliers in the data sets. It most cases they were included in the regression analysis as there was no strong evidence of their invalidity. However, three data points were removed from the set. One data point was from site EF35 in 1992 which had a negative value for zinc load. This being an impossibility, it was stricken. This reduced the number of data points for the regression to twenty-nine (number of data points are shown in each regression table in chapter 5, REGRESSION RESULTS). The other two data points were suspicious at the time of database construction. Since they did indeed end up showing very peculiar metal loads (due to data entry error), they were also stricken. One was from EF35 in 1991 which left twenty data points for this regression and the other was from AR65 in 1992 leaving thirty data points for the regression.

Examination of Metal Trends

Figures 3(a-d) and 4(a-d) display yearly changes for EF35 and AR65 for considered metals. The data points corresponding to the first 170 days are from water samples taken in 1991. The data set between the 345th and the 520th day is from samples taken in 1992. The plots of metal concentration in this section all have the same units, mg/L.

Figure 3a indicates a seasonal trend in zinc concentration for the first year of sampling at site EF35 (days 0-170). After the installation of the treatment plant, (approximately days 200-300) the seasonal trend is dampened and the zinc concentration is decreased. The treatment plant at the Leadville Drain had a significant impact on the amount of zinc passing through site EF35.

Figure 3b shows a decline for iron concentrations after the installation of the water treatment plant. This plot shows that a seasonal pattern remains after treatment although not as well defined.

Figure 3c shows an increase of sodium concentrations after treatment. This is acceptable since sodium hydroxide is used at the Leadville Drain treatment plant to help remove some of the heavy metals. The seasonal pattern that is exhibited in the sodium is likely due to the fact that there is a variable amount of stream flow.

Figure 3d illustrates the seasonal patterns for a constituent for which water treatment had little or no effect. Calcium is not considered an environmental or health hazard and is thus not treated. Calcium loads are also a simple relationship to model with a tight fit. This is included in this report as an example of a model for which the constituents are not affected due to water treatment.

Site AR65 is much farther down stream from the Leadville Drain treatment plant. However, there is another treatment plant above site AR65, the Leadville YAK Tunnel

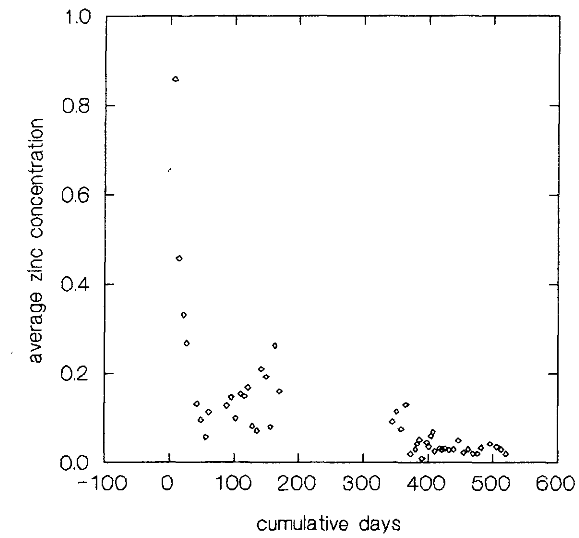

Figure 3a. Zinc concentrations during 1991 and 1992 for site EF35.

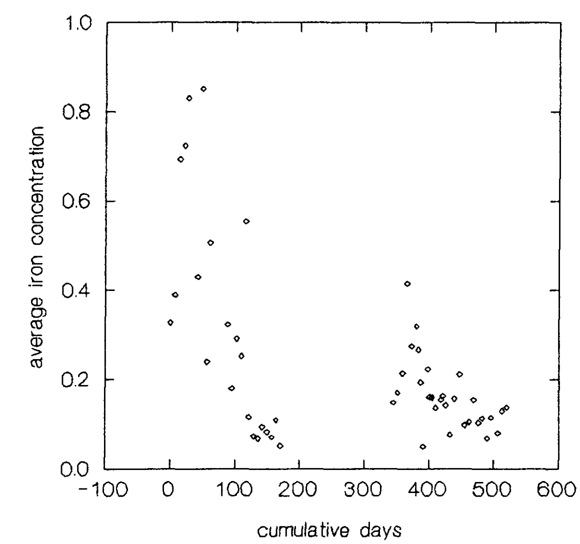

Figure 3b. Iron concentrations during 1991 and 1992 for site EF35.

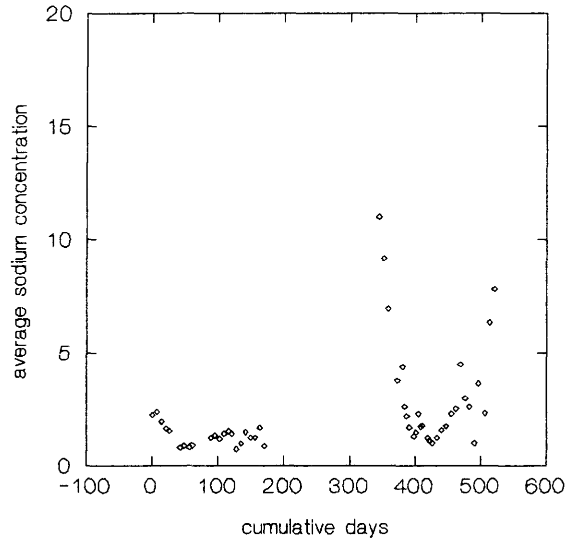

Figure 3c. Sodium concentrations during 1991 and 1992 for site EF35.

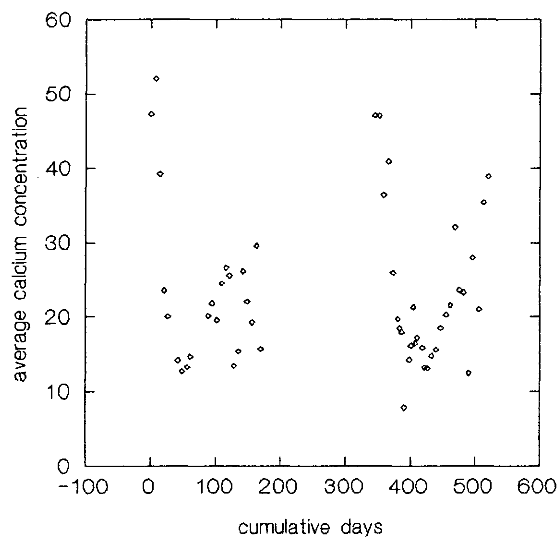

Figure 3d. Calcium concentrations during 1991 and 1992 for site EF35.

water treatment plant (see figure 1). This second treatment plant is located at the top of California Gulch, a highly contaminated (mostly iron) tributary to the Arkansas river (USFWS 1993). Therefore, the combined impact of the two treatment plants is expected to be observed at site AR65. Due to the California Gulch running through mine tailings below the Leadville YAK Tunnel, more contaminants are likely coming into the waterway from this tributary.

The seasonal trend has returned in 1992 indicating that zinc is entering the Arkansas below the Leadville Drain according to the water flow. The added zinc may be coming from the California Gulch (see figure 1) (USFWS 1993).

Figure 4b exhibits a definite decrease in iron concentration after treatment with some seasonal attributes still existing. The scaling for the average iron concentration is higher than that for EF35. This indicates that iron is entering the water system below the Leadville Drain treatment plant increasing the overall iron concentration. This is in spite of the two treatments (Leadville Drain and YAK Tunnel). A possible source of iron are the California Gulch (see figure 1) (USFWS 1993).

Figure 4c shows a slight increase in sodium for 1992. This is brought about by the use of sodium hydroxide in the treatment of metals at the Leadville Drain treatment plant.

This is not as pronounced as for site EF35 since AR65 is not as close to a treatment plant. It is interesting to note that there is a seasonal pattern in the concentration of sodium for 1991 at site AR65 but not at site EF35. The seasonal fluctuations in the sodium concentration for 1992 is likely to be attributed to the use of sodium at the treatment plant being seasonal or to the dilution of a constant source of sodium by seasonal variations in flow. The plot of calcium concentration in figure 4d is an example of seasonal variability where treatment did not have an effect.

Figure 4d is an example of an untreated constituent. However, note that there is less calcium at site AR65 than at site EF35.

So far, metal concentrations have been examined for individual sites. In order to make a site comparison, metal loads are measured. The metal loads are calculated as described in equation 2.1 Rather than examining metal concentration, a comparison of metal loads (which takes into account the different stream flows of the sites) for the two sites is displayed in figures 5a through 5e.

All the plots comparing EF35 with AR65 show EF35 as having a significantly lower metal load than AR65. A reasonable conclusion would be that the metals are coming

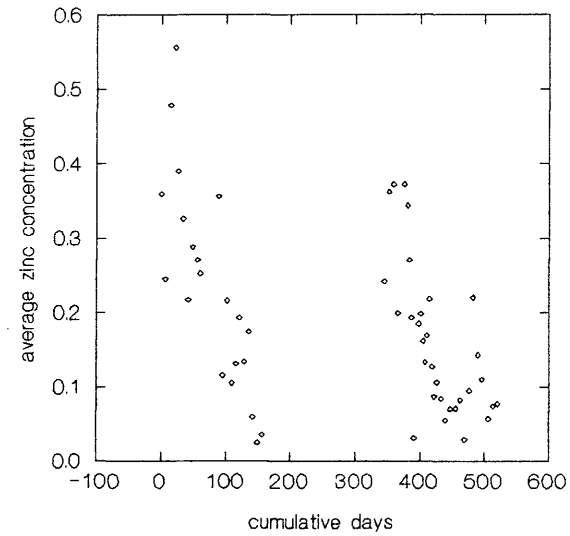

Figure 4a. Zinc concentrations during 1991 and 1992 for site AR65.

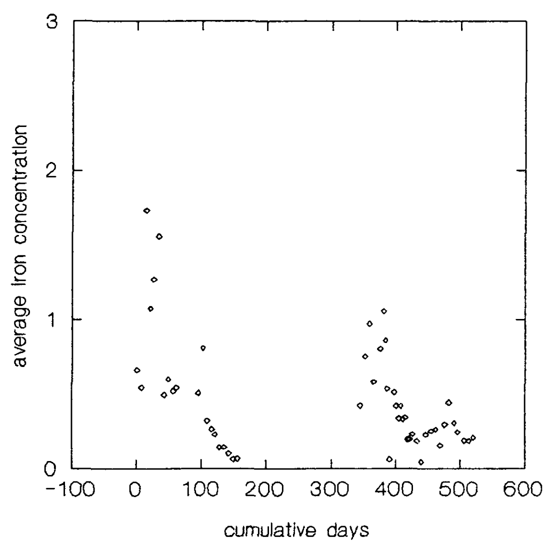

Figure 4b. Iron Concentrations during 1991 and 1992 for site AR65.

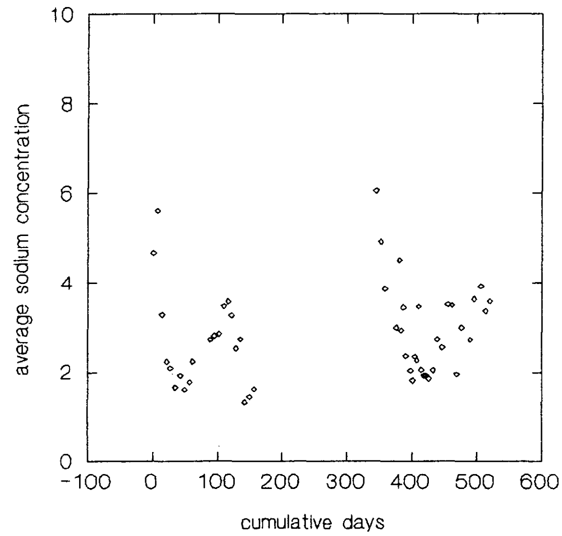

Figure 4c. Sodium concentrations during 1991 and 1992 for site AR65.

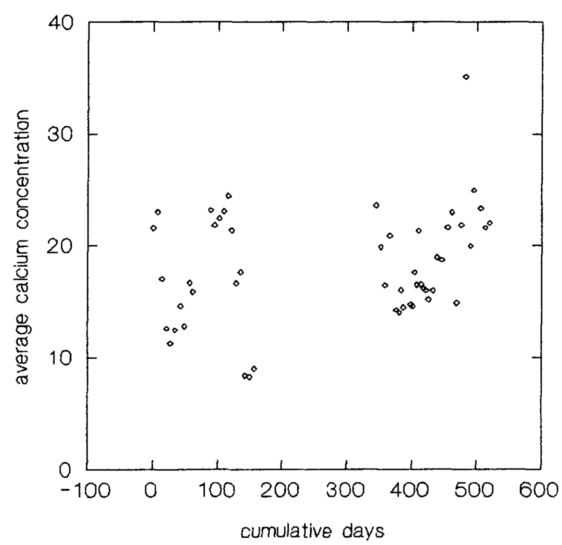

Figure 4d. Calcium concentrations during 1991 and 1992 for site AR65.

into the Arkansas downstream from site EF35. There are several tributaries coming into the Arkansas river between EF35 and AR65 where the metals may be coming from. A seasonal trend is also much more obvious at site AR65 signifying the dependence upon flow. Examining the scale for metal loads between 1991 and 1992 indicates the effect of the water treatment plants on the metal loads. Yearly comparisons of the trend is shown in figures 6a through 6d. Note the significant changes in the vertical scales between the different figures.

A plot to compare turbidity for the two sites is shown in figure 5e to see if turbidity behaves like either of the two metals to predict (iron or zinc). Interestingly, turbidity shows no difference between the sites.

Due to the close proximity of EF35 to the Leadville Drain treatment plant, the yearly changes are more obvious (figures 6a through 6d). However, site AR65 also shows the benefit of water treatment. The zinc load has been significantly reduced as well as some reduction in the iron load.

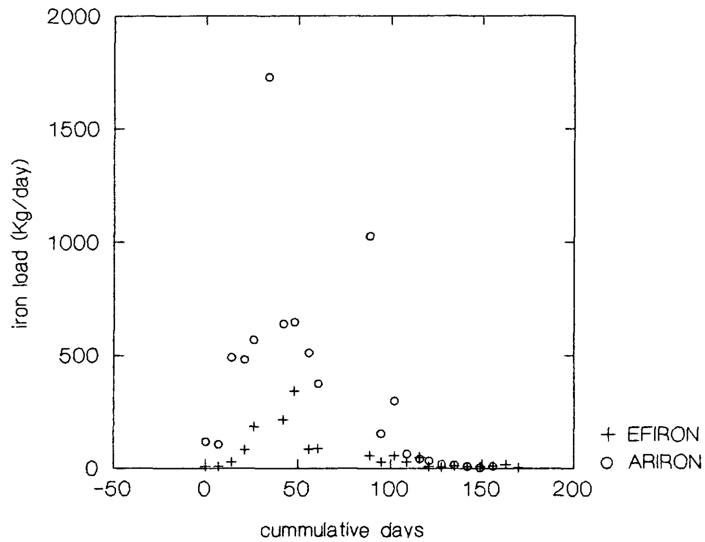

Figure 5a. Comparative plot for iron loads for EF35 and AR65 in 1991.

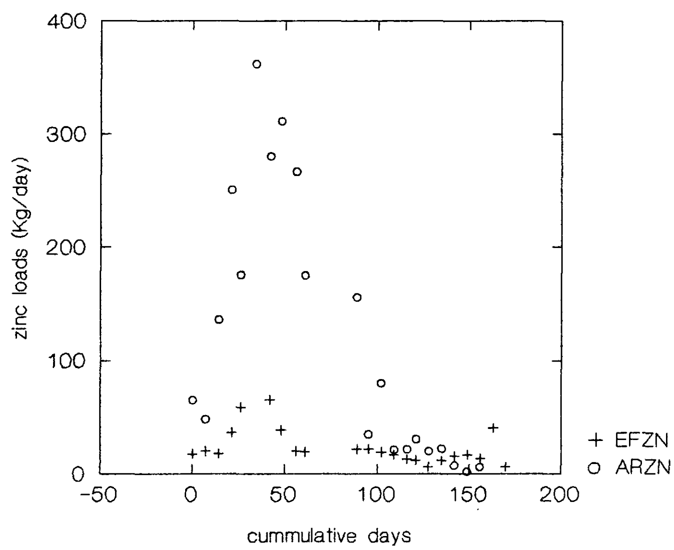

Figure 5b. Comparative plot for zinc loads for EF35 and AR65 in 1991.

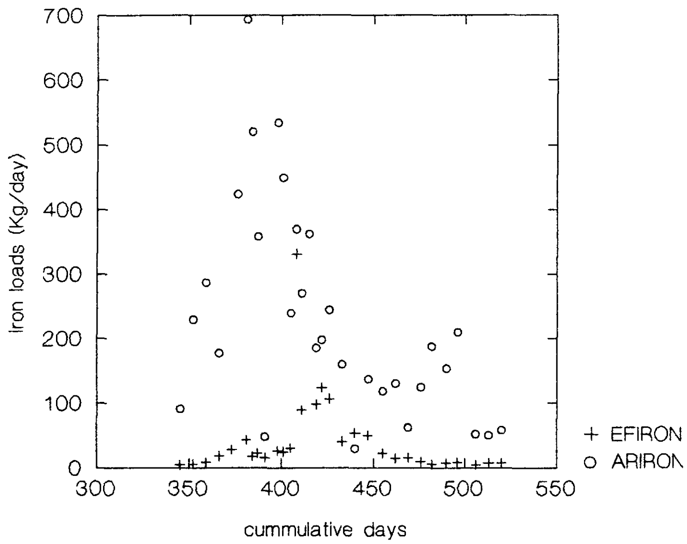

Figure 5c. Comparative plot for iron loads for EF35 and AR65 in 1992.

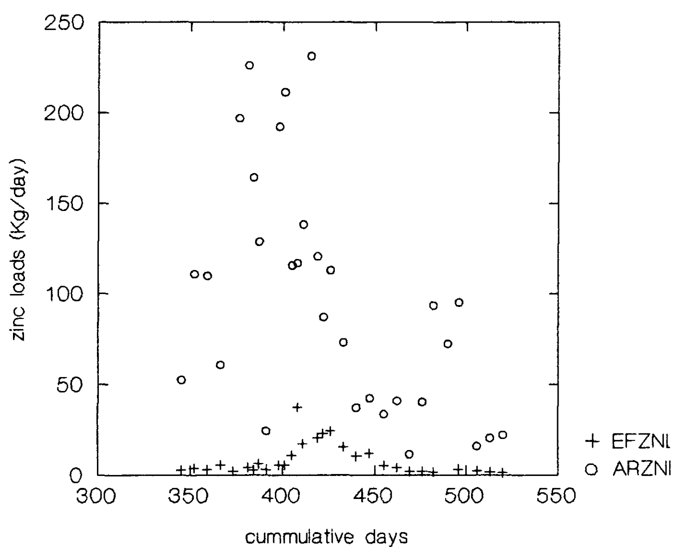

Figure 5d. Comparative plot for zinc loads for EF35 and AR65 in 1992.

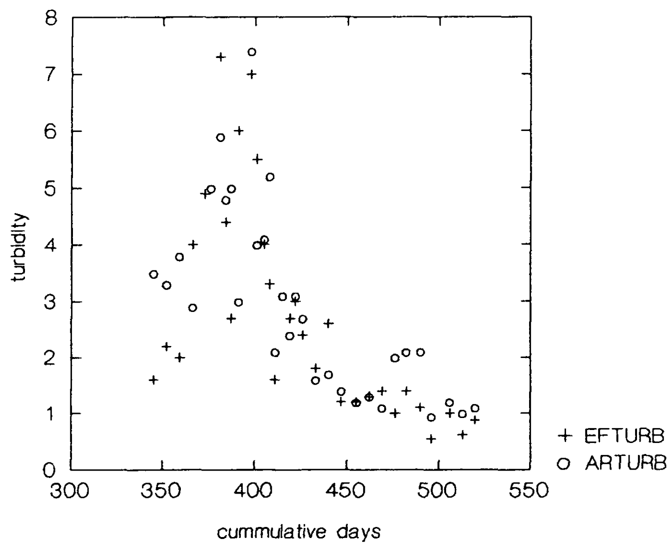

Figure 5e. Comparative turbidity plot for EF35 and AR65 in 1992.

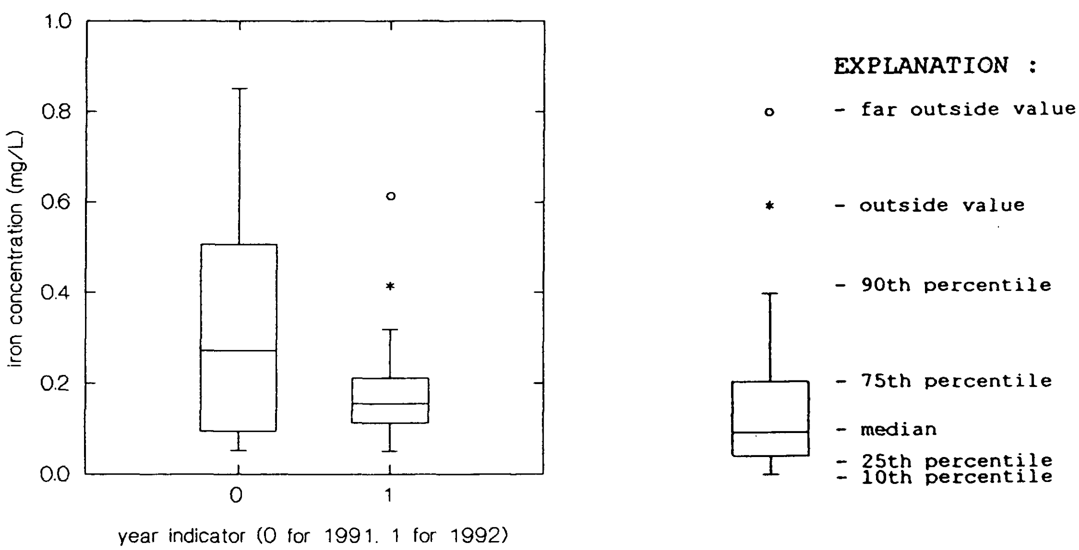

Figure 6a. Yearly comparison of iron concentration for site EF35.

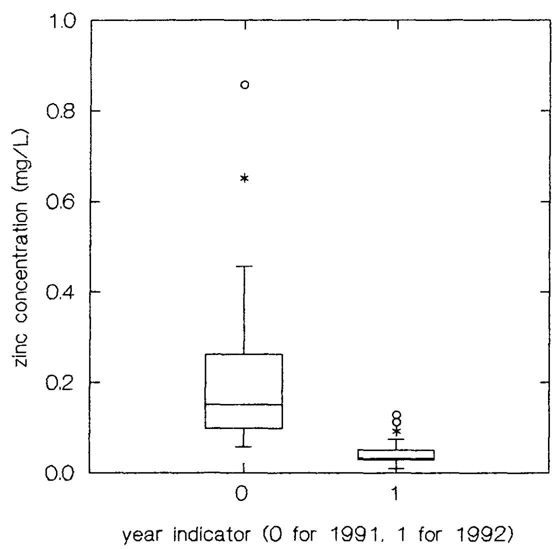

Figure 6b. Yearly comparison of zinc concentration for site EF35.

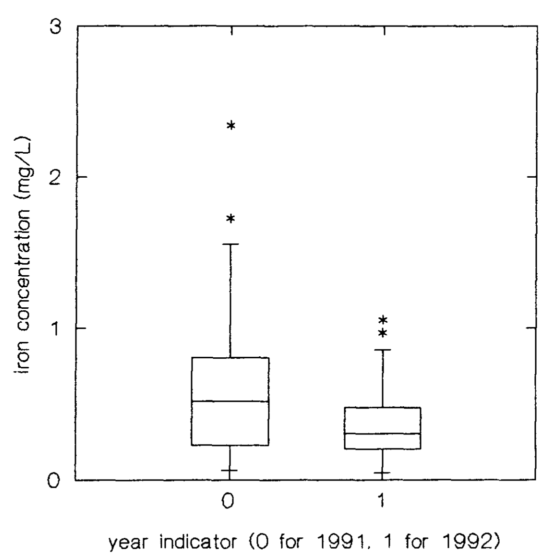

Figure 6c. Yearly comparison of iron concentration for site AR65.

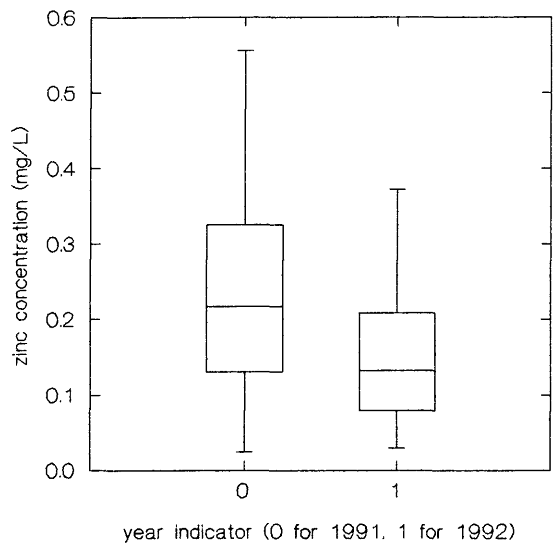

Figure 6d. Yearly comparison of zinc concentration for site AR65.

Examination of Predictor Variable Trends

The seasonal fluctuations in metal concentrations leads to the examination of the predictor variables for a seasonal relationship. Figures 7a through 8d are plots examining the relationships of stream discharge, conductivity, iron particulate, and cumulative days for both sites.

Figure 7a indicates that conductivity behaves seasonally and is therefore a possible predictor for heavy metal loads.

Figure 7b shows a seasonal pattern for stream discharge and is another possible predictor for the modeling of the heavy metals. Note that there is a slight increase in the discharge for 1992 during the high flow period. This is not significant enough to be concerned that 1991 and 1992 did not exhibit representative stream discharge. In fact, because stream discharge is greater in 1992 than in 1991, slightly larger metal loads would be expected in 1992 if there were no water treatment intervention.

Figure 7c shows a time series during 1991 and 1992 for iron particulate. The use of iron particulate was shown to be useful in predicting metal loads using regression techniques by Wetherbee and Kimball (Wetherbee and Kimball 1991).

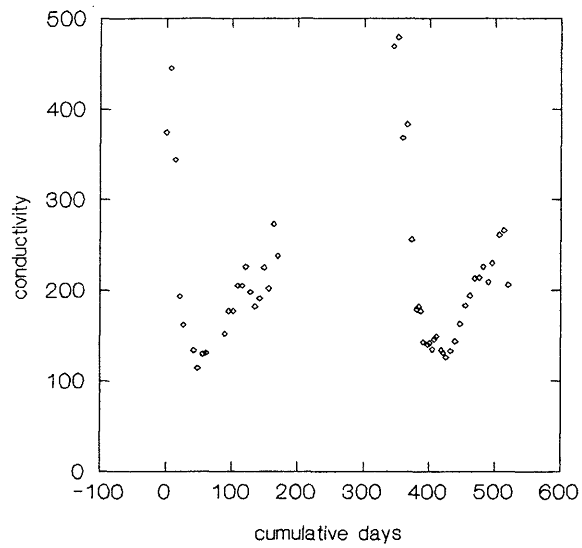

Figure 7a. Conductivity during 1991 and 1992 for site EF35.

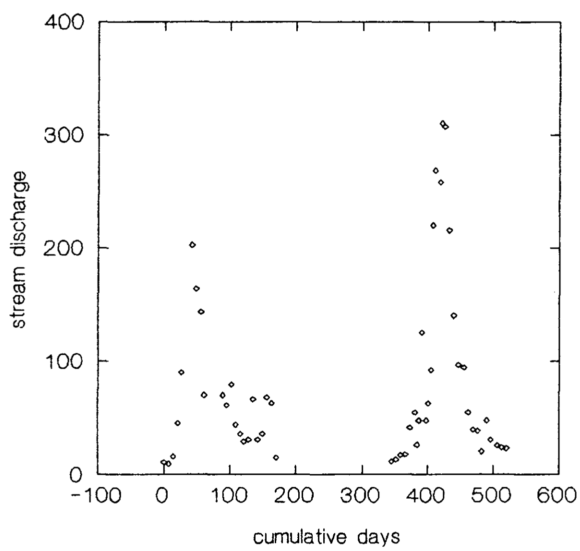

Figure 7b. Stream discharge during 1991 and 1992 for EF35.

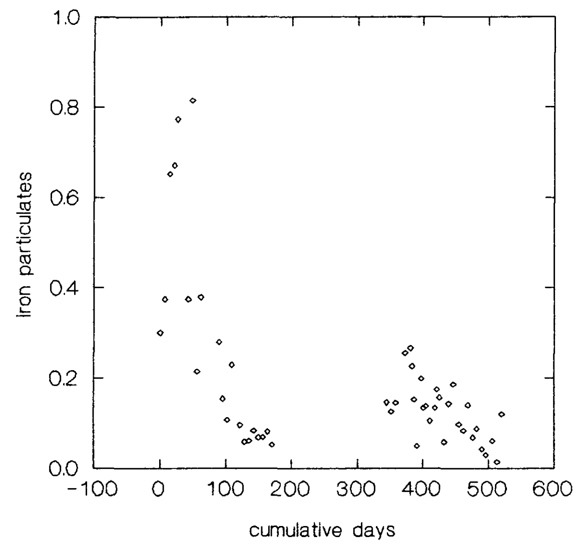

Figure 7c. Iron particulate during 1991 and 1992 for EF35.

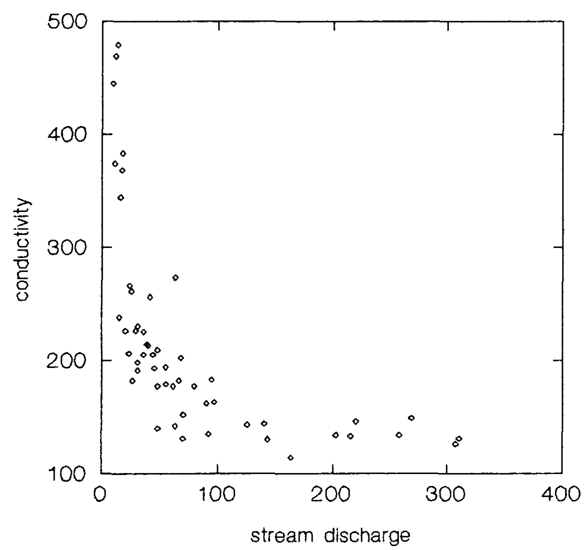

Figure 7d. Correlating stream discharge and conductivity for site EF35.

The high correlation between stream discharge and conductivity in figure 7d cautions against possible multicollinearity (Pearson correlation is -0.593). One of these variables may be enough to predict metal loads.

Figure 8a shows conductivity for site AR65 behaving similarly to conductivity at site EF35 (see figure 7a). Conductivity for site AR65 does not get as high during the low flow periods as it does for site EF35. This is probably because EF35 is directly below a high conductivity tributary (the Leadville Drain). Whereas, AR65 is not -- all high conductivity inputs to AR65 are diluted by the flow of more tributaries.

Sites AR65 and EF35 (figures 8b and 7b) show very similar characteristics regarding stream discharge patterns. Naturally, AR65 has a higher stream discharge.

The scale for iron particulate in figure 8c shows AR65 to have higher concentrations than for EF35 (see figure 7c). However, there is a significant decrease in 1992. There are three data points which show a measurement of zero for iron particulate in 1992.

Figure 8d indicates a relationship between stream discharge and conductivity for site AR65. The Pearson correlation is -0.605. This is a high enough correlation to

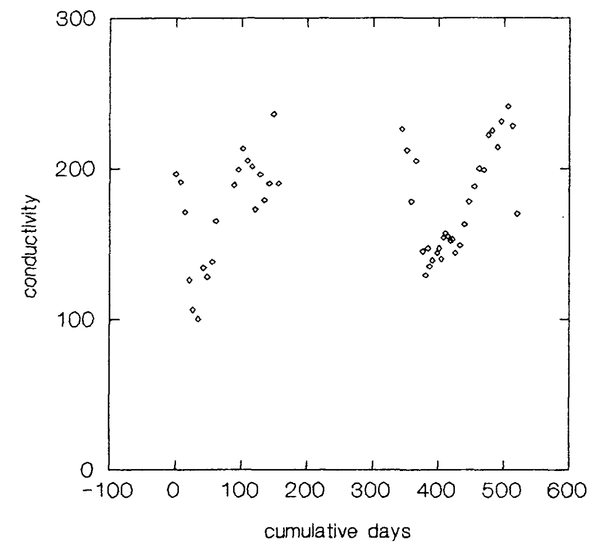

Figure 8a. Conductivity during 1991 and 1992 for site AR65.

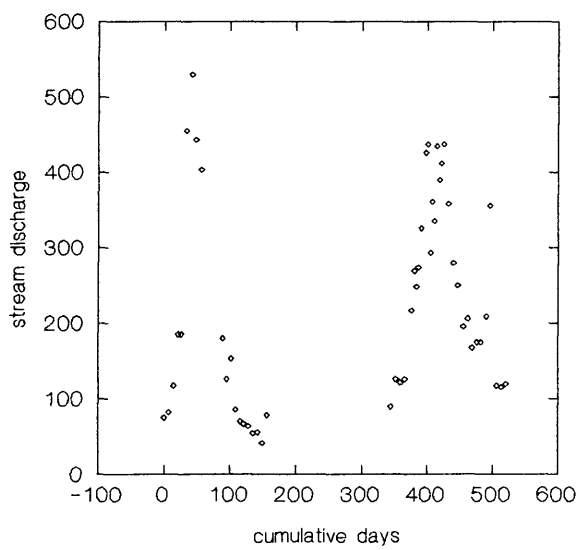

Figure 8b. Stream discharge during 1991 and 1992 for AR65.

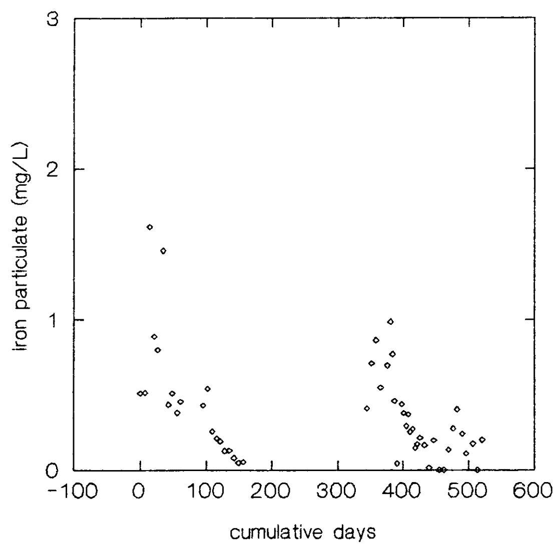

Figure 8c. Iron particulate during 1991 and 1992 for AR65.

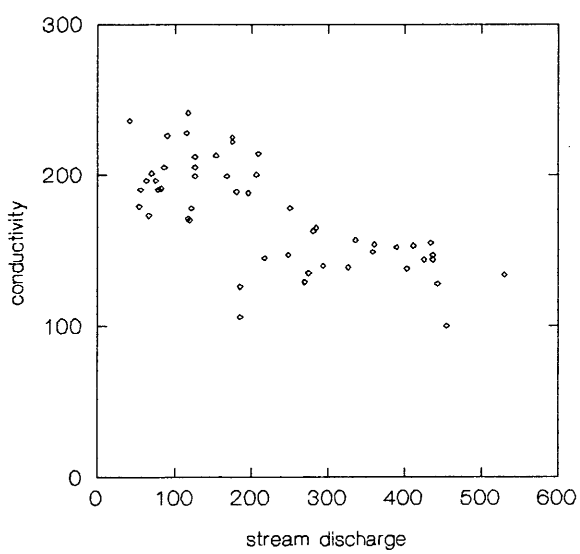

Figure 8d. Correlating stream discharge and conductivity for AR65.

be wary of using both stream discharge and conductivity in the same model.

Conductivity and stream discharge are inversely related. During high flow periods (high stream discharge) the conductivity of the water is lower. Since stream discharge is obviously seasonal, either conductivity or stream discharge will be helpful in modeling the metal load (stream discharge is generally the stronger predictor in this study). Iron particulate also shows a pattern similar to zinc and iron concentrations. Again, this relationship is magnified at EF35. This is because of more natural variability at AR65.

Chapter 5

MODEL BUILDING

After examination of the possible predictor variables available, the model was narrowed down to three or four predictors. Using stepwise regression provided by the SYSTAT software package, the best contributors for the model were selected. The selection of the variables is based on the adjusted correlation coefficient (adjusted R^2) which determines whether the added complexity to the model for the new variable outweighs the benefit of a tighter fit (see equation 3.4). The significance of the addition or removal of a variable is called an alpha (α) value. The F^* statistic (F^* is sometimes referred to as the F-ratio) as defined on page 18 is used to indicate whether the variable should be included or excluded. The F^* values can be found in the regression tables displayed in chapter 6, REGRESSION RESULTS. If the fit can be significantly improved by the addition (or removal) of a variable, (determined by the α value), then it enters (or exits) the model. The α value can be chosen when using the SYSTAT regression package. Lower values such as α = .05 are used for predictor variables that are highly correlated. The values used were alpha-to-enter and alpha-to-remove values of no greater than

0.15. When the predictor variables are relatively independent, these are commonly used values for choosing the predictor variables.

A simple multiple variable linear model produced good fits for all the combinations of site, year, and metal. However, the plots of the residuals from the regression indicated a problem of heteroscadasticity in most of the models. Also, the normal probability plot did not look linear for many models signifying that the assumption of normally distributed data was being violated. A plot of the residuals against cumulative days was examined to confirm there was no time dependent relationship (where there is, another dependent variable for time is added to the model).

Transforming all the variables with the natural logarithm function rectified both problems of hetero-scedasticity and non-normality. This is a well known transformation in the field of hydrology and was expected to work well. However, there were a few data points that had a value of zero for iron particulate (a very strong predictor). This was not a reason to exclude these data points as it simply meant all the iron measured was in dissolved form. Since a log transformation cannot be applied to a zero value, a similar transformation was considered as a substitute -- square root. This transformation worked as well and sometimes even better when solving the problems of heteroscedasticity and non-normality. Figures 9a through 10c show the effects of transforming the variables in order to meet the necessary requirements of homoscedasticity and normality. Several other similar power transformations could be used as well. For ease of use, the printed regression results for this project are obtained using a square root transformation on all the variables in the models.

There is a noticeable spread in the residuals in figure 9a as the estimates get larger. This is an indication of heteroscedasticity. Once the logarithm transformation is applied (figure 9b), the residuals fall in a "more random" way removing the indication of heteroscedasticity. The square root transformation also provided the desired result (figure 9c).

Figures 10a, 10b, and 10c show the effects of the transformations on the probability plots. Without any transformation, the data looks as though there were three different sets of data. The logarithm transformation works very well as shown by the straight line in the plot. The square root transformation significantly improves the normality of the data.

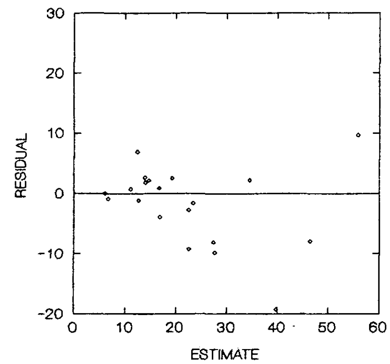

Figure 9a. Plot of residuals verses estimated values for predicting zinc load regression at site EF35 1991 before transformation.

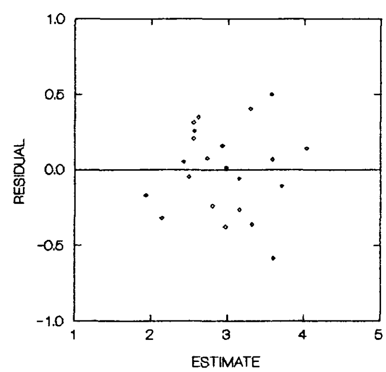

Figure 9b. Plot of residuals verses estimated values for predicting zinc load regression at site EF35 1991 after a natural log transformation.

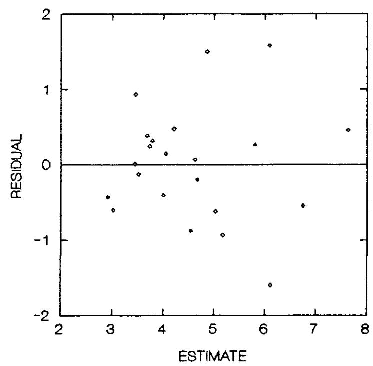

Figure 9c. Plot of residuals verses estimated values for predicting zinc load regression at site EF35 1991 after a square root transformation.

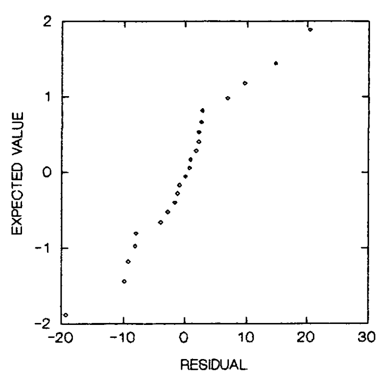

Figure 10a. Probability plot for predicting zinc loads for site EF35 in 1991 before transformation.

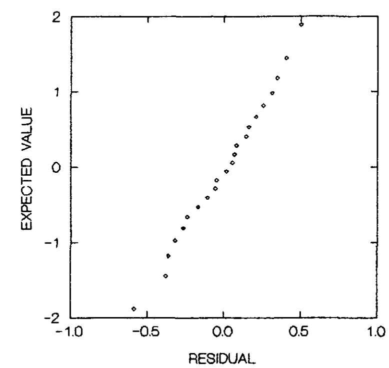

Figure 10b. Probability plot for predicting zinc loads for site EF35 in 1991 after natural log transformation.

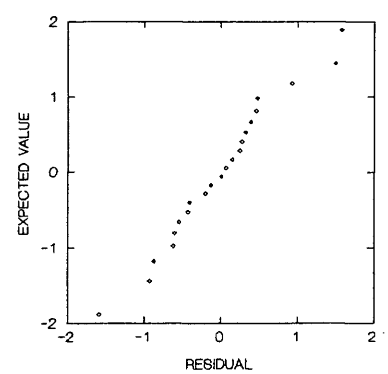

Figure 10c. Probability plot for predicting zinc loads for site EF35 in 1991 after a square root transformation.

Chapter 6

REGRESSION RESULTS

Several models provided adequate fits, therefore, choices of the final models were made based on simplicity, noncollinearity of independent variables, whether mini-monitor data could be used solely, and, whether turbidity could be used in place of iron particulate (for 1992 models). The regressions were done using stepwise techniques allowing for all possible predictors to be in the model based on an alpha-to-enter and alpha-to-exit of 0.15. This often resulted in complicated models with too many variables. Although these models are included, a degree of multicollinearity may be a problem here. Interactive stepwise regression techniques were also employed in order to choose variables that were not too highly correlated and to produce models with certain desirable variables.

Models for Site EF35

Table 1 displays the only model chosen for zinc loads at site EF35 for 1991. This model is very satisfactory since the correlation matrix for the independent variables showed no inter-correlation:

PEARSON CORRELATION MATRIX*

	SQRFEPAR	SQRQ	SQRTEMP
SQRFEPAR	1.000		
SQRQ	0.226	1.000	
SQRTEMP	-0.225	0.127	1.000

* SQRFEPAR, square root of iron particulate; SQRQ, square root of stream discharge; SQRTEMP, square root of water temperature

No interactive efforts were pursued since the correlation coefficient (R^2) for this model is adequate.

Table 1. Stepwise regression for zinc load at site EF35 in 1991.

DEP VAR: ZINC N: 21 MULTIPLE R: 0.913 SQUARED MULTIPLE R: **0.833**

ADJUSTED SQUARED MULTIPLE R: .803 STANDARD ERROR OF ESTIMATE: 0.662

VARIABLE *	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	4.184	0.863	0.000		4.850	.15E-03
FEPART	1.954	0.686	0.305	0.858	2.849	0.011
Q	0.364	0.056	0.691	0.876	6.518	.53E-05
TEMP	-1.246	0.289	-0.455	0.886	-4.314	.47E-03

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	37.138	3	12.379	28.227	.790152E-06
RESIDUAL	7.456	17	0.439		

* FEPART, iron particulate; Q, Stream discharge; TEMP, water temperature.

Table 2 also gives a satisfactory model. The coefficient of correlation is very high indicating a good fit for the data.

Since the given variables are not intercorrelated (multicollinear), and other possible additions to the model would cause inter-correlation, no other models are displayed for this data set. Note that the water temperature coefficient has borderline significance (see p-value in table 2). Note that the p-values are two tailed.

Table 2. Stepwise regression for iron load at site EF35 in 1991.

DEP VAR:IRON N: 21 MULTIPLE R: 0.985 SQUARED MULTIPLE R: **0.970**

ADJUSTED SQUARED MULTIPLE R: .965 STANDARD ERROR OF ESTIMATE: 0.853

VARIABLE *	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-8.843	1.111	0.000		-7.963	.39E-06
FEPART	11.542	0.883	0.591	0.858	13.069	.27E-09
Q	1.043	0.072	0.649	0.876	14.498	.53E-10
TEMP	0.756	0.372	0.090	0.886	2.031	0.058

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	401.434	3	133.811	184.059	.370592E-12
RESIDUAL	12.359	17	0.727		

* FEPART, iron particulate; Q, Stream discharge; TEMP, water temperature.

Table 3a shows a high coefficient of correlation, however, iron particulate and turbidity may cause an inter-correlation problem (Pearson correlation coefficient is -0.53). Thus, an additional model is displayed in Table 3b that examines the results without the turbidity variable. Given the choice between iron particulate and turbidity, results are generally better when iron particulate is used. A slight change in the coefficients for iron particulate and for stream discharge is noted when turbidity is removed. This is indicative of the correlation between iron particulate and turbidity. Since the coefficients do not deviate dramatically, the model displayed in Table 3a may suffice, depending upon the degree of stability desired. The possibility of using turbidity rather than iron particulate was examined. Unfortunately, the coefficient for the turbidity variable was not significantly different from zero and the R^2 value fell to 0.787 (i.e., this was basically a model using only flow as a predictor).

Table 3a. Stepwise regression for zinc load at site EF35 in 1992.

DEP VAR:ZINC N: 29 MULTIPLE R: 0.950 SQUARED MULTIPLE R: **0.903**

ADJUSTED SQUARED MULTIPLE R: .891 STANDARD ERROR OF ESTIMATE: 0.431

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-0.404	0.299	0.000		-1.351	0.189
FEPART	4.017	0.736	0.404	0.707	5.458	.11E-04
Q	0.249	0.018	0.859	0.977	13.635	.44E-12
TURB	-0.438	0.176	-0.185	0.706	-2.495	0.020

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	43.225	3	14.408	77.593	.844991E-12
RESIDUAL	4.642	25	0.186		

* FEPART, iron particulate; Q, Stream discharge; TURB, turbidity.

Table 3b. Interactive (removal of turbidity predictor) stepwise regression for zinc load at site EF35 in 1992.

DEP VAR:ZINC N: 29 MULTIPLE R: 0.937 SQUARED MULTIPLE R: **0.879**

ADJUSTED SQUARED MULTIPLE R: .870 STANDARD ERROR OF ESTIMATE: 0.472

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-0.698	0.301	0.000		-2.318	0.029
FEPART	3.044	0.684	0.306	0.983	4.450	.14E-03
Q	0.246	0.020	0.847	0.983	12.304	.24E-11

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	42.069	2	21.035	94.327	.120792E-11
RESIDUAL	5.798	26	0.223		

* FEPART, iron particulate; Q, Stream discharge.

Table 4a. Stepwise regression for iron load at site EF35 in 1992.

DEP VAR:IRON N: 29 MULTIPLE R: 0.958 SQUARED MULTIPLE R: **0.918**

ADJUSTED SQUARED MULTIPLE R: .908 STANDARD ERROR OF ESTIMATE: 1.060

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-15.508	4.467	0.000		-3.472	0.002
CUM	0.502	0.197	0.175	0.673	2.550	0.017
FEPART	15.186	1.825	0.577	0.660	8.319	0.000
Q	0.585	0.045	0.743	0.974	13.027	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	325.676	3	108.559	96.537	0.000
RESIDUAL	29.238	26	1.125		

* CUM, cumulative days (seasonal variable); FEPART, iron particulate; Q, Stream discharge.

The stepwise regression (shown in table 4a) for iron at EF35 for 1992 may be somewhat unstable. This is because cumulative days and iron particulate have a correlation coefficient of 0.572 for the EF35 data in 1992. Due to the possible instability of the model, an additional model is examined. Table 4b is a display of the regression results when the seasonal variable (cumulative days) is removed from the model. The coefficients for iron particulate and stream discharge are affected by the removal of the seasonal variable. The model in table 4b still provides a high R^2 value and is therefore a dependable model.
The possibility of replacing iron particulate with turbidity was examined for this model but was not included because the results were very poor. The p-values for this model showed that the turbidity variable (as well as the constant value) was not significantly different from zero. Also, the R^2 value was much lower (0.69).

Table 4b. Interactive (removal of CUM predictor) stepwise regression results for iron load at site EF35 in 1992.

DEP VAR:IRON N: 29 MULTIPLE R: 0.947 SQUARED MULTIPLE R: **0.897**

ADJUSTED SQUARED MULTIPLE R: .889 STANDARD ERROR OF ESTIMATE: 1.163

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-4.240	0.716	0.000		-5.924	0.000
FEPART	12.525	1.643	0.476	0.980	7.622	0.000
Q	0.594	0.049	0.754	0.980	12.085	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	318.365	2	159.182	117.595	0.000
RESIDUAL	36.548	27	1.354		

* FEPART, iron particulate; Q, Stream discharge.

Models for Site AR65

Table 5a is a display of stepwise regression results for zinc loads at site AR65 for 1991. Due to the variety of variables in the model, two possible inter-correlation problems surfaced. The correlation coefficient between stream discharge (Q) and specific conductivity (COND) in this instance is 0.697. The correlation coefficient between cumulative days (CUM) and iron particulate (FEPART) is 0.476. Since the R^2 value is very high, the model can be reduced to fewer variables and still be a very good model.

Table 5b shows the results when the seasonal variable (CUM) is removed from the model. The coefficients of the remaining variables did not alter greatly, so the seasonal variable may be left in the model. However, the R^2 value is still very high without the seasonal variable. It is also noted that the adjusted R^2 value indicates that the added variables do not penalize the model significantly.

Table 5c examines the results for the removal of specific conductivity from the model. The p-value for the constant term in the model becomes very high suggesting there may be no need for the constant.

A very simple model is displayed in Table 5d with very good results. Iron particulate and stream discharge alone prove to be good predictors for zinc in 1991.

Table 5a. Stepwise regression results for zinc load at site AR65 in 1991.

DEP VAR:ZINC N: 21 MULTIPLE R: 0.985 SQUARED MULTIPLE R: **0.970**

ADJUSTED SQUARED MULTIPLE R: .963 STANDARD ERROR OF ESTIMATE: 1.075

VARIABLE *	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	11.913	4.126	0.000		2.888	0.011
COND	-0.866	0.266	-0.227	0.382	-3.262	0.005
CUM	-0.200	0.087	-0.126	0.616	-2.294	0.036
FEPART	3.928	0.914	0.240	0.592	4.296	0.001
Q	0.634	0.073	0.590	0.400	8.673	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	605.574	4	151.394	130.891	0.000
RESIDUAL	18.506	16	1.157		

* COND, specific conductance; CUM, cumulative days (seasonal variable); FEPART, iron particulate; Q, Stream discharge.

Table 5b. Interactive (removal of CUM predictor) stepwise regression results for zinc load at AR65 in 1991.

DEP VAR:ZINC N: 21 MULTIPLE R: 0.980 SQUARED MULTIPLE R: **0.961**

ADJUSTED SQUARED MULTIPLE R: .954 STANDARD ERROR OF ESTIMATE: 1.203

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	11.855	4.614	0.000		2.569	0.020
COND	-1.023	0.287	-0.268	0.409	-3.563	0.002
FEPART	4.925	0.899	0.302	0.765	5.478	0.000
Q	0.617	0.081	0.575	0.404	7.591	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	599.488	3	199.829	138.134	0.000
RESIDUAL	24.593	17	1.447		

* COND, specific conductance; FEPART, iron particulate; Q, stream discharge.

Table 5c. Interactive (removal of COND predictor) stepwise regression results for zinc load at site AR65 for 1991.

DEP VAR:ZINC N: 21 MULTIPLE R: 0.975 SQUARED MULTIPLE R: **0.951**

ADJUSTED SQUARED MULTIPLE R: .942 STANDARD ERROR OF ESTIMATE: 1.346

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-0.904	1.574	0.000		-0.574	0.573
FEPART	4.002	1.144	0.245	0.592	3.498	0.003
Q	0.800	0.066	0.745	0.778	12.192	0.000
CUM	-0.272	0.105	-0.172	0.659	-2.588	0.019

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	593.267	3	197.756	109.101	0.000
RESIDUAL	30.814	17	1.813		

* FEPART, iron particulate; Q, stream discharge; CUM, cumulative days (seasonal variable).

Table 5d. Interactive (removal of CUM and COND predictors) stepwise regression results for zinc loads at site AR65 for 1991.

DEP VAR:ZINC N: 21 MULTIPLE R: 0.965 SQUARED MULTIPLE R: **0.931**

ADJUSTED SQUARED MULTIPLE R: .924 STANDARD ERROR OF ESTIMATE: 1.545

VARIABLE *	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-4.370	0.949	0.000		-4.606	0.000
FEPART	5.480	1.137	0.336	0.788	4.818	0.000
Q	0.820	0.075	0.763	0.788	10.963	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	581.127	2	290.564	121.763	0.000
RESIDUAL	42.953	18	2.386		

* FEPART, iron particulate; Q, stream discharge.

Models for iron loads for site AR65 in 1991 are viewed in tables 6a through 6c. The stepwise regression utilized almost all the possible predictors (all except temperature). It has already been concluded that conductivity and stream discharge are correlated. The correlation between cumulative days and pH is borderline significant as well as the relation between cumulative days and iron particulate. Although the complete stepwise regression model is included, it is not recommended due to its complexity.

The model without the specific conductance (COND) predictor was attempted but it was inadequate. From examining the p-values of the coefficients of this model, it was determined that the coefficients for cumulative days and pH were not significantly different from zero.

Table 6b displays the model removing CUM and pH. The constant value here is not significantly different from zero as well as COND becoming borderline.

The simple yet very adequate model is shown in table 6c. Again, iron particulate and stream discharge are shown to be very strong predictors.

Table 6a. Stepwise regression results for iron load at site AR65 in 1991.

DEP VAR:IRON N: 21 MULTIPLE R: 0.991 SQUARED MULTIPLE R: **0.983**

ADJUSTED SQUARED MULTIPLE R: .977 STANDARD ERROR OF ESTIMATE: 1.635

VARIABLE *	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	41.115	26.262	0.000		1.566	0.138
COND	-1.284	0.426	-0.174	0.342	-3.012	0.009
CUM	0.425	0.160	0.138	0.422	2.659	0.018
FEPART	20.170	1.423	0.637	0.564	14.176	0.000
PH	-13.127	8.531	-0.063	0.669	-1.539	0.145
Q	0.951	0.112	0.456	0.390	8.454	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	2308.390	5	461.678	172.769	0.000
RESIDUAL	40.083	15	2.672		

* COND, specific conductance; CUM, cumulative days (seasonal variable); FEPART, iron particulate; Q, Stream discharge.

Table 6b. Interactive (removal of CUM and pH predictors) stepwise regression results for iron load at site AR65 in 1991.

DEP VAR:IRON N: 21 MULTIPLE R: 0.987 SQUARED MULTIPLE R: **0.975**

ADJUSTED SQUARED MULTIPLE R: .970 STANDARD ERROR OF ESTIMATE: 1.863

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	1.960	7.145	0.000		0.274	0.787
COND	-0.848	0.445	-0.115	0.409	-1.908	0.073
FEPART	18.265	1.393	0.576	0.765	13.116	0.000
Q	1.001	0.126	0.481	0.404	7.949	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	2289.493	3	763.164	219.965	0.000
RESIDUAL	58.981	17	3.469		

* COND, specific conductance; FEPART, iron particulate; Q, Stream discharge.

Table 6c. Interactive (removal of CUM, pH, and COND predictors) stepwise regression results for iron load at site AR65 in 1991.

DEP VAR:IRON N: 21 MULTIPLE R: 0.985 SQUARED MULTIPLE R: **0.970**

ADJUSTED SQUARED MULTIPLE R: .966 STANDARD ERROR OF ESTIMATE: 1.995

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	-11.498	1.225	0.000		-9.386	.23E-07
FEPART	18.725	1.469	0.591	0.788	12.749	.19E-09
Q	1.169	0.097	0.561	0.788	12.109	.44E-09

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	2276.861	2	1138.430	286.144	.227596E-13
RESIDUAL	71.613	18	3.979		

* FEPART, iron particulate; Q, Stream discharge.

Models for zinc loads at site AR65 for 1992 are shown in tables 7a and 7b. The stepwise regression in table 7a utilized both pH and stream discharge which have a Pearson correlation of 0.774. It may also be problematic to the model to include iron particulate with either pH or stream discharge (Pearson correlation's of 0.634 and 0.52, respectively).

Table 7b shows the results for interactively choosing the variables with the highest partial correlation in the first step. This is a very good model as it is very simple and utilizes the turbidity predictor. It also provided a better R^2 value than the stepwise (non-interactive) regression technique. The caution here is that there is a slight correlation between pH and turbidity.

The usual model of using iron particulate and stream discharge was also examined. Although this is a safe choice for the predictor variables, the R^2 value dropped to 0.799.

Table 7a. Stepwise regression results for zinc load at AR65 in 1992.

DEP VAR:ZINC N: 30 MULTIPLE R: 0.932 SQUARED MULTIPLE R: **0.869**

ADJUSTED SQUARED MULTIPLE R: .853 STANDARD ERROR OF ESTIMATE: 1.298

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	75.720	21.570	0.000		3.510	0.002
PH	-25.684	6.924	-0.482	0.300	-3.709	.99E-03
FEPART	5.368	1.261	0.412	0.539	4.256	.24E-03
Q	0.281	0.106	0.302	0.390	2.650	0.014

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	289.688	3	96.563	57.279	.136773E-10
RESIDUAL	43.831	26	1.686		

* FEPART, iron particulate; Q, Stream discharge.

Table 7b. Interactive (choice of highest partial correlation) stepwise regression results for zinc load at AR65 in 1992.

DEP VAR:ZINC N: 30 MULTIPLE R: 0.934 SQUARED MULTIPLE R: **0.872**

ADJUSTED SQUARED MULTIPLE R: .863 STANDARD ERROR OF ESTIMATE: 1.256

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	101.773	14.040	0.000		7.249	.85E-07
PH	-33.885	4.681	-0.635	0.614	-7.239	.87E-07
TURB	2.783	0.618	0.396	0.614	4.507	.11E-03

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	290.934	2	145.467	92.230	.856648E-12
RESIDUAL	42.585	27	1.577		

* TURB, turbidity.

Table 8 shows the stepwise regression results for iron loads for 1992. Turbidity proved to be a better predictor than iron particulate. There is a possible problem with the slight correlation between pH and turbidity. Several other models were examined but they did not prove to be as adequate.

Table 8. Stepwise regression results for iron load at site AR65 for 1992.

DEP VAR:IRON N: 30 MULTIPLE R: 0.905 SQUARED MULTIPLE R: **0.819**

ADJUSTED SQUARED MULTIPLE R: .806 STANDARD ERROR OF ESTIMATE: 2.299

VARIABLE*	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	104.175	25.703	0.000		4.053	0.000
PH	-34.906	8.569	-0.425	0.614	-4.074	0.000
TURB	6.250	1.131	0.577	0.614	5.528	0.000

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	646.874	2	323.437	61.188	0.000
RESIDUAL	142.720	27	5.286		

* TURB, turbidity.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

Data was obtained from the Environmental Protection Agency for the purpose of validating the regression models. The data received was very sparse as there were only one or two data points with the required information. This data set was not large enough to use for model validation. Although this step is omitted, the models should be considered satisfactory since the predictor variables have been shown to fit other hydrological data for the same purpose (Wetherbee and Kimball 1991). The format of the models is also known in the field of hydrology (Cain 1987).

A summary of all the regression equations is found in tables 9a through 10b. Tables 9b and 10b show that there are very simple models available in 1992 for both sites. This is likely due to the fact that the added water treatment plant removed some of the variability allowing for a simple model to fit the data.

Given that the water system does not change dramatically, the regression results show that iron and zinc can be successfully predicted given certain known parameters. For example, if zinc load needs to be predicted in 1993 at site EF35, a reasonable approximation should be attainable from knowing iron particulate and stream discharge (see table 10b, second equation).

The equations displayed in tables 9b and 10b are for future predictions of iron and zinc respectively. Tables 9a and 10a are provided for comparison purposes only. There are three equations available for iron prediction: two for site EF35 and one for site AR65. In the case of site EF35, the prediction should be made with the first equation available in table 9b under EF35 if the time variable CUM is known. If not, the second equation in table 9b under EF35 is used.

For zinc prediction, there are two equations available for each site. If turbidity is known for site EF35, the first equation in table 10b should be used. If not, use the second one. At site AR65, if iron particulate is known as well as stream discharge, the first equation is used. Otherwise, turbidity must be available to use the second equation.

In order to use a model, it must be remembered that all the variables have been transformed using a square root. An example of how to predict the zinc load at site AR65 (using the first model) is as follows: The first equation shown in table 10b under site AR65 is interpreted as (see eq. 3.1 for a detailed explanation):

$$Zn' = 75.72 - 12.68 * X_1' + 5.37 * X_2' + 0.28 * X_3'$$

where:

$Zn' = \sqrt{Zn}$,

$X_1' = \sqrt{X_1} = \sqrt{pH}$,

$X_2' = \sqrt{X_2} = \sqrt{Fepart}$, and

$X_3' = \sqrt{X_3} = \sqrt{Q}$.

Thus, the value obtained for zinc load must be squared. This gives a value for the level of zinc load at site AR65.

Nonintervention of the water system will make the predictions possible. The addition of the Leadville Drain treatment plant was an example of an intervention that altered the linear regression models. This is seen when comparing the regression equations between 1991 and 1992 in tables 9a through 10b. The difference seen between the two sites is also an example of the models being site specific. Prediction of metal loads at other sites could be accomplished by a similar approach used in this study.

Table 9a. Regression equations for iron load prediction in 1991.*

	1991									
	EF35				AR65					
Fe	β_0	β_1	β_2	β_3	β_0	β_1	β_2	β_3	β_4	β_5
	-8.84	11.54	1.04	0.76	41.12	-1.28	0.43	20.17	-13.13	0.95
		X_1	X_2	X_3		X_1	X_2	X_3	X_4	X_5
		Part	Q	Temp		Cond	Cum	Part	pH	Q
					β_0	β_1	β_2	β_3		
					1.96	-0.85	18.27	1.00		
						X_1	X_2	X_3		
						Cond	Part	Q		
					β_0	β_1	β_2			
					-11.50	18.73	1.17			
						X_1	X_2			
						Part	Q			

Table 9b. Regression equations for iron load prediction in 1992.

	1992						
	EF35				AR65		
Fe	β_0	β_1	β_2	β_3	β_0	β_1	β_2
	-15.51	0.50	15.19	0.59	104.2	-34.91	6.25
		X_1	X_2	X_3		X_1	X_2
		Cum	Part	Q		pH	Turb
	β_0	β_1	β_2				
	-4.24	12.53	0.59				
		X_1	X_2				
		Part	Q				

* This shows one model for EF35 and three models for AR65. Note some beta values are negative.

Table 10a. Regression equations for zinc load prediction in 1991.*

	1991								
	EF35				AR65				
Zn	β_o	β_1	β_2	β_3	β_o	β_1	β_2	β_3	β_4
	4.18	1.95	0.36	−1.25	11.91	−0.87	−0.20	3.92	0.63
		X_1	X_2	X_3		X_1	X_2	X_3	X_4
		Part	Q	Temp		Cond	Cum	Part	Q
					β_o	β_1	β_2	β_3	
					11.86	−1.02	4.93	0.62	
						X_1	X_2	X_3	
						Cond	Part	Q	
					β_o	β_1	β_2	β_3	
					−0.90	4.00	0.80	−0.27	
						X_1	X_2	X_3	
						Part	Q	Cum	
					β_o	β_1	β_2		
					−4.37	5.48	0.82		
						X_1	X_2		
						Part	Q		

Table 10b. Regression equations for zinc load prediction in 1992.

	1992							
	EF35				AR65			
Zn	β_o	β_1	β_2	β_3	β_o	β_1	β_2	β_3
	−0.40	4.02	0.25	0.44	75.72	−12.68	5.37	0.28
		X_1	X_2	X_3		X_1	X_2	X_3
		Part	Q	Turb		pH	Part	Q
	β_o	β_1	β_2		β_o	β_1	β_2	
	−0.70	3.04	0.25		101.8	−33.89	2.78	
		X_1	X_2			X_1	X_2	
		Part	Q			pH	Turb	

* This shows one model for EF35 and four models for AR65. Note that there are some negative betas.

Based on the criteria discussed in chapter 3, METHODOLOGY OF MODEL DEVELOPMENT, the modeling of the zinc and iron loads was successful for the two sites examined. The success of the modeling was largely due to the availability of certain predictor variables. The mini-monitor data alone did not provide "good fits", however, simple models were found using iron particulate and turbidity.

The models provided allow for the prediction of iron and zinc loads without the expensive and time consuming lab analysis of direct measurements. For future study, other contaminants should also be predicted using similar regression techniques. Other sites suspected of being highly contaminated are also likely candidates for this type of study.

REFERENCES CITED

Cain, Doug. 1987. Relations of Specific Conductance to Streamflow and Selected Water-Quality Characteristics of the Arkansas River Basin, Colorado. Water-Resources Investigations Report 87-4041. Denver, C.O.: U.S. Geological Survey.

Environmental Protection Agency. 1986. Quality Criteria for Water 1986. Washington, D.C.: Office of Water Regulation and Standards.

Garbarino, J.R. and Taylor, E.T. 1985. Recent Developments and Applications of Inductively Coupled Plasma Emission Spectroscopy to Trace Elemental Analysis of Water. vol. 4. Orlando, F.L.: Academic Press, Inc.

Horowitz, Arthur J. 1991. A Primer on Sediment-Trace Element Chemistry. 2nd. ed. Chelsea, M.I.: Lewis Publishers, Inc.

Kimball, Briant A. 1987. "Overview of the Upper Arkansas River Surface-Water Toxics Study Near Leadville, Colorado". U. S. Geological Survey Toxic Substances Hydrology Program -- Surface-Water Contamination: Proceedings of the Technical Meeting, Denver, Colorado, February 2-4, 1987. Open-File Report 87-764.

Neter, John; Wasserman, William; Kutner, Michael H. 1990 Applied Linear Statistical Models: Regression, Analysis of Variance, and Experimental Designs. 3rd ed. Boston, M.A.: Richard D. Irwin, Inc.

NOVA. 1990. "Poison in the Rockies". Public Television Jan. 9, 1990. produced by Christopher McLeod and Robert Lewis.

Rantz, S.E. and others. 1982. Measurement and Computation of Streamflow: Volume 1 Measurement of Stage and Discharge and Volume 2 Computation of Discharge. Geological Survey Water-Supply Paper 2175. Washington, D.C.: United States Government Printing Office.

United States Department of Agriculture, Forest Service Pamphlet. 1993. Acid Drainage From Mines on the National Forests: A Management Challenge. Program Aid 1505.

United States Fish and Wildlife Service, Ecological Services, Golden, Colorado and Colorado Department of Natural Resources, Division of Wildlife, Habitat Section, Denver, Colorado. 1993. Assessment of the Trout Population in the Upper Arkansas River Basin of Central Colorado. Golden, C.O.: Colorado State Office Ecological Services.

Wetherbee, Gregory A. and Kimball, Briant A. 1991. "Use of Environmental Variables to Estimate Metal Loads in Streams, Upper Arkansas River Basin, Colorado". U. S. Geological Survey Toxic Substance Hydrology Program. Water-Resources Investigations Report 91-4034. 398-406.

APPENDIX A: DATA SET FOR SITE EF35

SITE	DATE	CUM	Q	pH	COND	TEMP	FELOAD	ZNLOAD	TURB	FEPART
EF35	910424.	0.	11.04	6.97	374.	5.0	8.834	17.587	---	.300
EF35	910501.	7.	9.46	8.39	445.	2.5	9.016	19.873	---	.375
EF35	910508.	14.	15.94	8.30	344.	3.5	27.031	17.825	---	.652
EF35	910515.	21.	45.26	8.80	193.	3.0	80.184	36.659	---	.671
EF35	910520.	26.	89.94	8.11	162.	6.5	182.889	58.762	---	.773
EF35	910605.	42.	202.60	8.71	134.	4.0	212.930	65.441	---	.375
EF35	910611.	48.	163.90	8.30	114.	10.0	341.305	38.502	---	.814
EF35	910624.	61.	69.87	7.94	131.	6.0	86.512	19.320	---	.379
EF35	910722.	89.	69.87	7.97	152.	7.0	55.224	21.884	---	.279
EF35	910728.	95.	61.26	7.88	177.	7.0	26.983	21.886	---	.154
EF35	910804.	102.	79.40	8.18	177.	12.0	56.539	19.235	---	.107
EF35	910811.	109.	43.99	8.23	205.	9.0	27.126	16.577	---	.229
EF35	910818.	116.	35.86	8.34	205.	10.0	48.613	12.987	---	.539
EF35	910823.	121.	28.97	8.28	226.	7.5	8.223	11.909	---	.095
EF35	910830.	128.	30.82	8.61	198.	10.0	5.505	6.184	---	.058
EF35	910906.	135.	66.32	8.55	182.	10.0	10.954	11.522	---	.061
EF35	910913.	142.	30.82	8.40	191.	6.0	7.089	15.837	1.13	.083
EF35	910920.	149.	35.86	8.34	225.	6.0	7.283	16.848	1.47	.068
EF35	910927.	156.	68.07	8.20	202.	5.0	11.826	13.325	---	.069
EF35	911004.	163.	62.91	8.26	273.	3.0	16.780	40.332	38.00	.081
EF35	911011.	170.	14.85	7.82	238.	8.0	1.890	5.814	69.00	.052
EF35	920403.	345.	11.47	8.21	469.	3.0	4.154	2.582	1.60	.146
EF35	920410.	352.	13.32	8.45	479.	4.0	5.541	3.716	2.20	.125
EF35	920417.	359.	17.10	8.15	368.	6.0	8.955	3.138	2.00	.145
EF35	920424.	366.	17.71	8.18	383.	5.0	17.985	5.634	4.00	.410
EF35	920501.	373.	41.53	8.25	256.	5.0	27.947	2.032	4.90	.255
EF35	920509.	381.	55.00	7.95	179.	4.5	42.933	4.038	7.30	.266
EF35	920512.	384.	26.36	8.21	182.	3.5	17.222	2.774	4.40	.226
EF35	920515.	387.	47.89	7.87	177.	4.0	22.734	6.094	2.70	.152
EF35	920519.	391.	125.40	7.86	143.	3.0	15.343	3.069	6.00	.049
EF35	920526.	398.	47.89	8.09	140.	5.8	26.133	5.391	7.00	.199
EF35	920529.	401.	62.91	7.85	142.	4.5	24.784	5.542	5.50	.134
EF35	920602.	405.	92.17	7.75	135.	4.8	30.673	10.826	4.00	.138
EF35	920605.	408.	220.00	8.03	146.	5.5	331.079	37.145	3.30	.589
EF35	920608.	411.	268.60	8.07	149.	5.5	89.388	17.089	1.60	.105
EF35	920616.	419.	258.30	8.01	134.	5.5	97.969	20.226	2.70	.134
EF35	920619.	422.	310.35	7.99	131.	8.0	123.787	22.783	3.00	.175
EF35	920623.	426.	307.40	7.87	126.	6.5	106.814	24.071	2.40	.157
EF35	920630.	433.	215.60	7.93	133.	7.0	40.623	15.300	1.80	.058
EF35	920707.	440.	140.50	7.76	144.	6.5	53.977	10.314	2.60	.143
EF35	920714.	447.	96.77	8.31	163.	8.0	49.964	11.840	1.20	.186
EF35	920722.	455.	94.45	8.26	183.	8.0	22.650	5.316	1.20	.097
EF35	920729.	462.	55.00	8.27	194.	7.0	14.131	4.038	1.30	.083
EF35	920805.	469.	39.77	8.21	213.	7.5	15.084	2.044	1.40	.140
EF35	920812.	476.	38.62	8.30	214.	7.5	9.734	1.985	1.00	.068
EF35	920818.	482.	20.29	8.25	226.	7.5	5.610	1.688	1.40	.087

EF35	920901.	496.	30.82	7.50	230.	4.8	8.635	3.205	.55	.029
EF35	920911.	506.	25.52	8.42	261.	6.0	4.996	2.248	1.00	.060
EF35	920918.	513.	23.93	7.76	266.	6.5	7.525	1.727	.62	.014
EF35	920925.	520.	23.17	7.91	206.	6.0	7.767	1.134	.88	.120

--- for turbidity means no record.

APPENDIX B: DATA SET FOR SITE AR65

SITE	DATE	CUM	Q	pH	COND	TEMP	FELOAD	ZNLOAD	TURB	FEPART
AR65	910424.	0.	74.83	7.08	196.	8.0	120.852	65.736	---	.511
AR65	910501.	7.	81.88	8.22	191.	10.0	108.796	49.088	---	.515
AR65	910508.	14.	117.00	8.40	171.	12.0	494.438	136.994	---	1.615
AR65	910515.	21.	184.90	8.56	126.	6.5	485.027	251.562	---	.887
AR65	910520.	26.	184.90	8.20	106.	7.0	571.897	176.456	---	.797
AR65	910528.	34.	454.70	8.16	100.	9.0	1730.172	362.724	---	1.456
AR65	910605.	42.	529.30	8.16	134.	9.0	642.418	281.058	---	.435
AR65	910611.	48.	443.00	8.28	128.	12.5	650.413	312.198	---	.510
AR65	910619.	56.	403.20	8.10	138.	10.7	514.034	267.377	---	.382
AR65	910624.	61.	283.80	8.22	165.	14.0	377.091	175.698	---	.456
AR65	910722.	89.	179.80	8.04	189.	12.0	1030.851	156.630	---	2.242
AR65	910728.	95.	125.60	8.29	199.	15.0	156.130	35.652	---	.430
AR65	910804.	102.	152.80	8.28	213.	15.0	302.112	80.763	---	.540
AR65	910811.	109.	85.52	8.34	205.	15.0	66.966	21.973	---	.256
AR65	910818.	116.	69.72	8.40	201.	15.0	45.210	22.349	---	.210
AR65	910823.	121.	66.40	8.37	173.	14.7	36.883	31.359	---	.190
AR65	910830.	128.	63.15	8.36	196.	17.0	21.943	20.707	---	.127
AR65	910906.	135.	53.84	8.40	179.	11.0	18.840	22.924	---	.130
AR65	910913.	142.	55.35	8.13	190.	11.0	13.544	7.991	3.90	.080
AR65	910920.	149.	41.37	8.34	236.	10.0	6.327	2.480	1.18	.048
AR65	910927.	156.	78.32	7.98	190.	11.0	13.032	6.708	---	.053
AR65	920403.	345.	89.22	8.65	226.	9.0	92.350	52.834	3.50	.409
AR65	920410.	352.	125.60	7.99	212.	10.0	230.815	111.258	3.30	.708
AR65	920417.	359.	121.30	8.16	178.	8.5	288.213	110.417	3.80	.863
AR65	920424.	366.	125.60	8.27	205.	11.5	178.874	61.161	2.90	.549
AR65	920504.	376.	216.80	7.81	145.	13.0	424.938	197.350	5.00	.695
AR65	920509.	381.	268.90	7.68	129.	8.0	694.846	226.351	5.90	.985
AR65	920512.	384.	248.10	7.81	147.	11.5	521.500	164.524	4.80	.770
AR65	920515.	387.	273.45	8.20	135.	11.5	358.989	129.143	5.00	.459
AR65	920519.	391.	325.60	7.84	139.	11.3	49.398	24.699	3.00	.043
AR65	920526.	398.	425.70	8.02	144.	12.5	535.428	192.712	7.40	.439
AR65	920529.	401.	437.10	7.91	147.	10.5	450.295	211.778	4.00	.379
AR65	920602.	405.	292.80	7.81	140.	13.0	240.738	116.070	4.10	.293
AR65	920605.	408.	360.60	7.86	154.	12.0	370.603	117.358	5.20	.370
AR65	920608.	411.	335.40	7.59	157.	10.5	271.660	138.702	2.10	.254
AR65	920612.	415.	434.25	7.73	155.	11.0	363.413	231.649	3.10	.273
AR65	920616.	419.	389.60	7.84	152.	11.0	186.857	121.076	2.40	.146
AR65	920619.	422.	411.60	8.18	153.	14.5	199.423	87.625	3.10	.171
AR65	920623.	426.	437.10	7.91	144.	12.0	246.004	113.376	2.70	.213
AR65	920630.	433.	358.05	8.22	149.	15.5	161.211	73.596	1.60	.165
AR65	920707.	440.	279.40	8.21	163.	13.5	31.450	37.603	1.70	.013
AR65	920714.	447.	249.55	8.54	178.	13.5	138.617	42.745	1.40	.197
AR65	920722.	455.	195.30	8.60	188.	14.5	119.953	33.931	1.20	.000
AR65	920729.	462.	205.90	8.48	200.	13.0	132.005	41.315	1.30	.000
AR65	920805.	469.	167.30	8.78	199.	13.5	63.659	11.872	1.10	.134
AR65	920812.	476.	174.70	8.24	222.	14.0	126.110	40.612	2.00	.274

AR65	920818.	482.	174.70	8.36	225.	11.5	188.951	94.048	2.10	.402
AR65	920826.	490.	208.60	8.42	214.	13.0	155.175	72.994	2.10	.240
AR65	920901.	496.	355.50	7.95	231.	10.5	211.388	95.690	.94	.107
AR65	920911.	506.	117.00	8.89	241.	14.0	53.538	16.319	1.20	.174
AR65	920918.	513.	114.90	8.70	228.	11.5	51.733	20.806	1.00	.000
AR65	920925.	520.	119.10	8.74	170.	10.0	59.745	22.441	1.10	.199

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