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Statistical Tools for Analyzing Water Quality Data

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1. Introduction

Water quality data are often collected at different sites over time to improve water quality management. Water quality data usually exhibit the following characteristics: non-normal distribution, presence of outliers, missing values, values below detection limits (censored), and serial dependence. It is essential to apply appropriate statistical methodology when analyzing water quality data to draw valid conclusions and hence provide useful advice in water management. In this chapter, we will provide and demonstrate various statistical tools for analyzing such water quality data, and will also introduce how to use a statistical software R to analyze water quality data by various statistical methods. A dataset collected from the Susquehanna River Basin will be used to demonstrate various statistical methods provided in this chapter. The dataset can be downloaded from website http://www.srbc.net/programs/CBP/nutrientprogram.htm.

2. Graphical analysis of water quality data

Graphs provide visual summaries of data, quickly and clearly describe important information contained in the data, and provide insight for the analyst into the data under scrutiny. Graphs will help to determine if more complicated modeling is necessary. In this section, three particularly useful graphical methods are presented: boxplots, scatter plots, and Q-Q plots. R codes for plotting graphs in the following subsections will be given in detail.

2.1 Boxplots

A boxplot is a very useful and convenient tool to provide summaries of a dataset and is often used in exploratory data analysis. A boxplot usually presents a dataset through five numbers: extreme values (minimum and maximum values), median (50th percentile), 25th percentile, and 75th percentile. It also indicates the degree of dispersion, the degree of skew, and unusual values of the data (outliers). Furthermore, boxplots can display differences

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between different populations without making any assumptions of the underlying statistical distribution. Boxplots of concentrations of total phosphorus (mg/L) at four stations from the Susquehanna River Basin from 2005 to 2010 are constructed (Fig. 1). R codes for constructing Fig. 1 are as follows:

```r
> yl<- "Concentrations of total phosphorus (mg/L)"
> boxplot(TP ~ Station, ylab = yl, data = dat, boxwex = 0.5, outline = TRUE)
```

In Fig. 1, it can be seen that the four stations have nearly identical median values, and outliers could be present at all four stations. The distributions are right skewed. Further details on construction of a boxplot can be found in McGill et al. (1978), and Tukey (1977). More details for plotting boxplots are available in Adler (2009), Crawley (2007), and Venables & Ripley (2002).

![Boxplots for total phosphorus at four stations at the Susquehanna River Basin](image)

**Fig. 1.** Boxplots for total phosphorus at four stations at the Susquehanna River Basin

### 2.2 Scatter plots

A scatter plot is a very useful summary of a set of bivariate data (two variables), usually drawn before obtaining a linear correlation coefficient or fitting a regression line. It can be used to detect whether the relationships between two variables are linear or curved, and aids the interpretation of the correlation coefficient or a regression model. Fig. 2 is a scatter plot of the concentration of total phosphorus (mg/L) versus instantaneous flow (feet$^3$/s) in log scale at Station 1.

```r
> xl<- "Instantaneous flow on log scale in cubic feet per second"
> plot(log(UNA$Flow), UNA$TP, xlab = xl, ylab = yl)
> points(log(UNA$Flow)[39], UNA$TP[39], col=2, pch =16)
> points(log(UNA$Flow)[18], UNA$TP[18], col=2, pch =16)
> points(log(UNA$Flow)[50], UNA$TP[50], col=2, pch =16)
```

![Scatter plot of total phosphorus versus instantaneous flow](image)
We can generate a scatter plot using the data from two stations and can also use the function 

\[ \text{xyplot} \text{(Venables & Ripley, 2002)} \] to split the data into different panels based on station (Fig. 3 (a), (b)).

```r
> plot(log(UNA$Flow), UNA$TP, xlab = xl, ylab = yl, type = "p", pch = 1, col = 1)
> points(log(CKL$Flow), CKL$TP, pch = 3, col = 2)
> legend(4.5, 0.3, c("Station 1", "Station 2"), pch = c(1, 3), col=c(1, 2))
> library(lattice)
> xyplot(TP ∼ log(Flow) | Station, data = dat, xlab = xl, ylab = yl, col = 1)
```

Concentration varies with natural log of instantaneous flow, as illustrated using a scatter plot. A linear regression model could be used to fit the data in Fig. 2, but true changes in slope are difficult to detect from only a scatter plot. Various methods have been developed to construct a central line to detect variation of slope locally in response to the data themselves, such as the locally weighted scatter plot smoothing (LOWESS) method (Fig. 4) (Cleveland et al., 1992).

```r
> plot(log(UNA$Flow), UNA$TP, xlab = xl, ylab = yl)
> lines(lowess((UNA$TP) ∼ log(UNA$Flow)), col=2)
```

### 2.3 Q-Q plots

A Q-Q plot presents the quantiles of a dataset against the quantiles of another dataset (Chambers et al., 1983; Gnanadesikan & Wilk, 1968). It can be used to determine whether two datasets come from populations with the same distribution. The greater the departure from the reference line, the greater the evidence to conclude that these two datasets come from populations with different distributions. If their distributions are identical, the Q-Q plot follows a straight line. Q-Q plots can be applied to compare the distribution of a sample
Fig. 3. Scatter plots of total phosphorus and instantaneous flow

(a) two stations

(b) four stations

Fig. 4. The data of Fig. 2 fitted with the locally weighted scatter plot smoothing method to a theoretical distribution (often a normal distribution). Therefore, Q-Q plots provide a very efficient way to tell how a sample distribution deviates from an expected distribution. The advantages of Q-Q plots are that (a) the sample sizes of two datasets do not need to be equal; (b) many distributional aspects can be simultaneously tested, such as shifts in location and scale and changes in symmetry; (c) the presence of outliers can also be detected. The functions `qqnorm` and `qqplot` can be used to construct a Q-Q plot (Adler, 2009; Crawley, 2007; Venables & Ripley, 2002). Fig. 5 (a) and (b) are two Q-Q plots to test whether the distributions of total phosphorus concentrations and the values of on the natural log scale at Station 1 are
normal, respectively.
> qqnorm(UNA$TP); qqline(UNA$TP, col = 2)
> qqnorm(log(UNA$TP)); qqline(log(UNA$TP), col = 2)

![Normal Q-Q Plot](image)

(a)

![Normal Q-Q Plot](image)

(b)

Fig. 5. A Q-Q plot of total phosphorus concentrations at Station 1 versus the standard normal distribution

Fig. 5 (a) indicates that the distribution of total phosphorus concentrations is skewed to the right. Fig. 5 (b) shows an S-shape, but there is not sufficient evidence to prove that the distribution of total phosphorus on the natural log scale is non-normal. Fig. 6 is a Q-Q plot comparing whether two sample datasets are from populations with a common distribution. Note that there are also a few outliers appearing (possible outliers are in red). Otherwise, the plot suggests that the two samples have the same distribution.

> qq <- qqplot(UNA$TP, CKL$TP, plot.it = TRUE, xlab = “Concentrations of total phosphorus at Station 1”, ylab = “Concentrations of total phosphorus at Station 2”)
> points(qq$x[85],qq$y[85], pch=16, col=2)
> points(qq$x[84],qq$y[84], pch=16, col=2)
> points(qq$x[83],qq$y[83], pch=16, col=2)

3. Water quality index

Sometimes it is difficult to assess water quality from a large number of water quality parameters. Traditional methods to evaluate water quality are based on the comparison of experimentally determined parameter values with an existing local normative, which does not provide a global summary on the spatial and temporal trends in the overall water quality (Debels et al., 2005; Kannel et al., 2007). To integrate complex water quality data and provide a simple and understandable tool for informing managers and decision-makers about the overall water quality status, various water quality indices (WQI) have been developed, which can be used to give a global vision on the spatial and temporal changes of the water quality. An early water quality index was proposed by Horton (1965), and then developed by Brown et al. (1970), Dojlido et al. (1994), McClelland (1974), and Pesce & Wunderlin (2000).
Water quality indices have been employed frequently in the public domain to assess water quality, such as the US National Sanitation Foundation Water Quality Index (Brown et al., 1970), the Canadian Water Quality index (CCME, 2001), the British Columbia Water Quality Index (Zandbergen & Hall, 1998) and the Oregon Water Quality Index (Cude, 2001). Main steps to derive a water quality index are as follows: select the most important water quality parameters (such as dissolved oxygen, total phosphorus, temperature); transform the parameters into a common scale; assign parameter weights; and aggregate scores to a single score. In this section, various water quality indices, such as those based on the weighted/unweighted arithmetic/geometric/harmonic mean functions, will be presented and compared. Their uses and limitations will be also discussed.

3.1 Weighted water quality indices

Water quality indices are usually obtained by assigning a suitable weight to each water quality parameter index and averaging them using some type of average functions. In this subsection, we consider three different weighted water quality indices. The water quality index proposed by Pesce & Wunderlin (2000) is:

\[ WQI_{SA} = k \sum_{i=1}^{n} \omega_i S_i, \]  

where \( n \) is the number of the water quality parameters, \( S_i \) is the score of the \( i \)th parameter, and \( \omega_i \) is the relative weight given to \( S_i \) satisfying \( \sum_{i=1}^{n} \omega_i = 1 \). \( k \) is a subjective constant representing the visual impression of river contamination. The value of \( k \) ranges from 0.25 (for highly contaminated water) to 1 (for water without contamination). \( WQI_{SA} \) tends to overestimate the pollution due to the use of a subjective constant, which is not correlated with the measured parameters (Kannel et al., 2007).
Let \( k = 1 \) in Equation (1). In general, we have the objective water quality index originally proposed by Horton (1965), hereafter called the weighted arithmetic water quality index. It has been used by many researchers (Brown et al., 1970; Prati et al., 1971; Sanchez et al., 2007):

\[
WQI_{WA} = \sum_{i=1}^{n} \omega_i S_i.
\]

The third water quality index is based on the weighted geometric mean function (Brown et al., 1970; McClelland, 1974), which is always smaller than \( WQI_{WA} \) if all values of \( S_i \) are positive:

\[
WQI_{WG} = \prod_{i=1}^{n} S_i^{\omega_i}.
\]

The above weighted water quality indices indicate that each water quality parameter may have different weights based on the importance of the water quality situation. This characteristic could be desirable when water quality indices are specific to the protection of aquatic life. However, when sensitivity to changes in each water quality parameter is more desirable than sensitivity to the most heavily weighted water quality parameter, such weighting could be unnecessary (Cude, 2001; Gupta et al., 2003; Landwehr & Deininger, 1976). Some unweighted water quality indices were therefore explored (Cude, 2001; Dojlido et al., 1994; Landwehr & Deininger, 1976) and are now introduced in the following subsection.

### 3.2 Unweighted water quality indices

In this subsection, we introduce three unweighted water quality indices. The first two are arithmetic/geometric water quality indices proposed by Landwehr & Deininger (1976),

\[
WQI_A = \frac{1}{n} \sum_{i=1}^{n} S_i,
\]

\[
WQI_G = \left( \prod_{i=1}^{n} S_i \right)^{1/n},
\]

which is a special case of (2) and (3) with \( \omega_i = 1/n \) for any \( i \), respectively. As with the relationship between \( WQI_{WG} \) and \( WQI_{WA} \), \( WQI_G \) is always lower than \( WQI_A \). The third is the harmonic square water quality index,

\[
WQI_H = \sqrt[2n]{\frac{1}{\sum_{i=1}^{n} S_i^2}},
\]

which has been suggested as an improvement over both \( WQI_{WA} \) and \( WQI_{WG} \) (Cude, 2001; Dojlido et al., 1994). Compared to \( WQI_{WA} \) and \( WQI_{WG} \), \( WQI_H \) is the most sensitive to changes in single water quality parameter (Cude, 2001).

### 3.3 Harkins’ water quality index

An objective water quality index was proposed by Harkins (1974), which is based on Kendall’s nonparametric multivariate ranking procedure.
\[
WQI_{HR} = \sum_{i=1}^{n} \frac{(R_i - R_{ic})^2}{\text{var}(R_i)},
\]

where
\[
\text{var}(R_i) = \frac{1}{12M} [(M^3 - M) - \sum_{j=1}^{k_i} (t_{ij}^3 - t_{ij})],
\]

\(R_i\) and \(R_{ic}\) correspond to the rank and control values of the \(i\)th water quality parameter, respectively. \(M\) is the number of water quality parameters plus the number of control values, \(t_{ij}\) is the number of elements involved in the \(j\)th tie encountered when ordering the measured values of the \(i\)th water quality parameter, and \(k_i\) is the total number of ties encountered in ranking the measurements of the \(i\)th parameter.

Landwehr & Deininger (1976) and Gupta et al. (2003) compared \(WQI_{HR}\) with water quality indices \(WQI_{WA}\), \(WQI_{WG}\), \(WQI_{G}\), and \(WQI_{A}\). Their results indicated that these five indices are correlated well with the opinions of experts, and although the five indices showed significant correlation with each other, \(WQI_{HR}\) was the lowest of the five. Therefore, they suggested adopting any of the four indices except \(WQI_{HR}\).

4. Methods for handling data below detection limits

One feature of water quality measurement is that some data will fall above or below the detection limit, and therefore not be captured, because of limitations of the measurement procedures or the analytical tools used in the laboratories. Data below a detection limit are also referred as left-censored data. There could also be multiple detection limits involved if an instrument is upgraded during the project period or data are combined from multiple laboratories. Even data below the detection limits are still of considerable importance because of the potential health hazard. The data below the detection limits complicate the analysis of the water quality data. Various strategies have been developed to analyze the data that fall below detection limits (Fu & Wang, 2011; Helsel, 1990; Shumway et al., 2002). In the following subsections, simple substitution methods, parametric methods, and nonparametric methods will be introduced.

4.1 Simple deletion/substitution methods

Simple deletion/substitution methods delete/replace the measurements below detection limits (DL) with fixed values, such as zero, \(1/2\text{DL}\), \(1/\sqrt{2}\text{DL}\) or \(\text{DL}\) (Helsel, 1990; Hornung & Reed, 1990). Hornung & Reed (1990) proposed using \(1/\sqrt{2}\text{DL}\) when the data are not highly skewed and \(1/2\text{DL}\) substitution otherwise. Hewett & Ganser (2007) found that \(1/2\text{DL}\) and \(1/\sqrt{2}\text{DL}\) perform well when the sample size is less than 20 and the percent censored is less than 45 percent. It is easy and convenient to use the substitution methods. However, all tend to be biased and cause a loss of information (El-Shaarawi & Esterby, 1992; Helsel & Cohn, 1988; Lubin et al., 2004). When the results strongly depend on the values being substituted, particularly for data with multiple detection limits (Shumway et al., 2002), the substitution methods are not generally suitable. In particular, when there is a high proportion of data below detection limits, results for standard errors are also far less desirable, and the biased standard errors may further distort the inference (Helsel, 1990; 1992; Shumway et al., 2002).
4.2 Parametric methods

Assume that the distribution of measurements is known, such as normal or lognormal. The data below the detection limits can be filled using values randomly selected from the distribution or replaced with their conditional expected values (conditional on being less than the detection limits) (Helsel, 1990). Suppose that there are \( n \) detected measurements \((y_1, \ldots, y_n)\) and \( m \) measurements below the detection limits \((c_1, \ldots, c_m)\). The likelihood function is

\[
L(\theta) = \prod_{i=1}^{n} f_{\theta}(y_i) \prod_{j=1}^{m} F_{\theta}(c_j),
\]

where \( \theta \) is a vector of parameters, \( f(\cdot) \) is the probability density function of \( y \), and \( F(\cdot) \) is the cumulative density function (c.d.f.) of \( y \). The parameter estimates of \( \theta \) and summary statistics can be obtained by the maximum likelihood method (ML) (Cohen, 1976; Cohn, 1988; Helsel, 1992). Results based on a lognormal distribution assumption by the maximum likelihood method can be easily obtained using statistic software R (NADA package) (Lee & Helsel, 2005). If the distributional assumption is appropriate and the sample size is large, the maximum likelihood method is the most efficient (Cohn, 1988; Helsel, 1992; Hewett & Ganser, 2007). To incorporate the covariate effects when analyzing the water quality data that fall below detection limits, the following regression models can be considered.

4.2.1 Tobit regression

Tobit regression model (Tobin, 1958) has been widely used to analyze censored data. The model can be written as

\[
\log(y_i^*) = \beta_0 + \beta_1 x_i + \epsilon_i
\]

where \( y^*_i \) is a latent variable and \( y_i = y_i^* \) if \( y_i^* > c_i \) and \( y_i = c_i \) otherwise. Random error term \( \epsilon_i \) follows a normal distribution \( N(0, \sigma^2) \). The likelihood function (8) can be written as

\[
L(\beta_0, \beta_1) = \prod_i \left[ \frac{1}{\sigma} \phi \left( \frac{\log(y_i) - \beta_0 - \beta_1 x_i}{\sigma} \right) \right]^{\delta_i} \prod_i \left[ \left( 1 - \phi \left( \frac{\log(c_i) - \beta_0 - \beta_1 x_i}{\sigma} \right) \right) \right]^{1-\delta_i},
\]

where \( \delta_i = 1 \) if \( y_i^* > c_i \) and \( \delta_i = 0 \) otherwise. The maximum likelihood estimates (MLE) of parameters can be obtained from the function `survreg` (survival package) and `vglm` (VGAM package) in R if the detection limit is a single number. An example to obtain MLE of parameters in a Tobit regression model \( \log(DP) = \beta_0 + \beta_1 \log(Flow) + \epsilon \) is given,

```r
> library(survival)
> fit<- survreg(Surv(log(DP), DP>=0.01, type = 'left') ~ log(Flow), data = UNA, dist = 'gaussian')
> summary(fit)
```

For multiple detection limits, the estimates can be derived by a Newton-Raphson algorithm. The Wald type test or the likelihood ratio test can be applied to test the group difference or covariate effects (by testing \( \beta = 0 \)). Tobit regression is also applicable when both the measurements of the response and covariate variable are with detection limits (Helsel, 1992). When the distribution is known and the error terms are homeostatic, the estimate derived by the maximum likelihood method is optimal (Helsel, 2005b).
4.2.2 Logistic regression

Let $\tilde{y} = 1$ if the response is above a detection limit $c$ and $\tilde{y} = 0$ otherwise. Assume that the probability of $\tilde{y} = 1$ is $p$, then $p = p(y > c)$. A binary logistic regression modeled as a linear function of covariate $x$ is given by

$$\log\left(\frac{p}{1-p}\right) = \alpha_0 + \alpha_1 x.$$ 

The likelihood function is

$$L(\alpha_0, \alpha_1) = \prod_i p_i^{\tilde{y}_i} (1 - p_i)^{1 - \tilde{y}_i},$$

where $p_i = \exp(\alpha_0 + \alpha_1 x_i) / [1 + \exp(\alpha_0 + \alpha_1 x_i)]$. The maximum likelihood estimates of parameters can be obtained from \texttt{glm} function in R. The significance of the covariate effect can be tested using the likelihood ratio statistic (Helsel, 1992). For multiple detection limits, the ordered logistic regression can be used. More details can be seen in Helsel (1992). An example to obtain parameter estimates from a logistic regression $\log(p/(1-p)) = \alpha_0 + \alpha_1 \log(\text{Flow})$ is given as follows, where $p = p(DP > 0.01)$.

```r
> UNA$DPd <- 1 - (UNA$DP<1) 
> logifit<- glm(DPd ~ log(Flow), data = UNA, family = binomial("logit"))
```

Parametric methods generally perform well for summary statistics when the dataset is large and the underlying distribution can be approximated by a known distribution. Specification of the underlying distribution of a dataset may be difficult in practical problems. The ML method does not work well when the distributional assumption is invalid or the sample size is small (<20) (Gleit, 1985; Helsel, 2005b; Helsel & Cohn, 1988). Furthermore, the ML method is sensitive to outliers, which usually exist in water quality data. An implementation of fully parametric methods is a robust and efficient semi-parametric regression method on order statistics (ROS) and will be introduced in the following subsection.

4.2.3 ROS method

The ROS method was provided by Helsel & Cohn (1988), which is a simple imputation method that fills in data below detection limits based on a probability plot of detections (Helsel & Cohn, 1988; Lee & Helsel, 2005; Shumway et al., 2002). It can be used to obtain summary statistics, plot modeled distributions, and predict values based on the modeled distributions (Fig. 7). The ROS method has been evaluated as one of the most reliable approaches for estimating summary statistics of data with multiple detection limits (Shumway et al., 2002). Lee & Helsel (2005) developed software implementation that performs the ROS method, and it is a part of the NADA library in statistical software R. R codes for Fig. 7 are as follows:

```r
> library(NADA)
> UNA<- UNA[!is.na(UNA$OP), ]
> UNA$CenOP<- UNA$OPrem == "<"
> rosop<- cenros(UNA$OP, UNA$CenOP, forwardT = "log", reverseT = "exp")
> plot(rosop, plot.censored = TRUE)
> lines(rosop, col = 2)
```
Fig. 7. A normal Q-Q plot for a ROS model. Solid circles are detected data. Open circles are modeled undetected values.

4.3 Nonparametric methods

Parametric and semi-parametric methods are based on the assumption of the underlying distribution of the data. Nonparametric methods provide an alternative that does not require specifying a distribution and filling in the data below detection limits. The nonparametric methods are generally used to analyze the right censored data. Left censored data can be converted into right-censored data by flipping the data over the largest observed value. Lee & Helsel (2007) provided software tools for direct analysis of data with multiple detection limits (left-censored data) by nonparametric modeling and hypothesis testing.

4.3.1 Kaplan-Meier

The Kaplan-Meier (K-M) method is the standard method for computing descriptive statistics of data that fall below detection limits (Helsel, 2005; Lee & Helsel, 2007). K-M method has been widely used in survival analysis, where it is employed with right-censored time-to-failure data. The K-M method can estimate the percentiles or c.d.f. for a dataset, and can test hypotheses. It can describe and compare the shapes of different datasets (Figs. 8 (a) and (b)).

```R
> KM<- cenfit(UNA$OP, UNA$CenOP)
> plot(KM)
> dat2<- dat2[!is.na(dat2$OP),]
> dat2$CenOP<- dat2$OPrem == "<"
> g2<- cenfit(dat2$OP, dat2$CenOP,dat2$Station)
> plot(g2,lty = c(1:3), col=c(1, 2, 4))
> legend(0.002, 0.8, c("Station 1","Station 2","Station 4"), lty = c(1:3), col=c(1, 2, 4))
```
Zhang et al. (2009) developed a nonparametric estimation procedure, and under a fixed detection limit and some mild conditions, they established the theoretical equivalence of three nonparametric test statistics: the Wilcoxon rank sum, the Gehan, and the Peto-Peto tests. Their simulation studies indicated that nonparametric methods work well for a range of small sizes and censoring rates (Zhang et al., 2009). For hypothesis testing with multiple detection limits, one robust method is to censor all data at the highest detection limit and then perform an appropriate nonparametric test (Helsel, 1992). This can result in a loss of information, however, the accelerated failure time (AFT) model can integrate the Gehan and logrank tests, incorporate covariate effects, and compare the differences between two/multiple data groups with multiple detection limits (Jin et al., 2006; Wei, 1992; Zhang et al., 2009).

4.3.2 AFT model

Assume that \(\{Y_i, i = 1, \ldots, N\}, \{C_i, i = 1, \ldots, N\}\) and \(\{X_i, i = 1, \ldots, N\}\) are measurements, detection limits and \(p \times 1\) covariate vector, respectively. Let \(\Delta_i = 1\) if \(Y_i\) is below the detection limit \(C_i\) and \(\Delta_i = 0\) otherwise. Let \(\tilde{Z}_i = \min\{−\log(Y_i), −\log(C_i)\}\); therefore \((\tilde{Z}_i, \Delta_i, X_i)\) are the observations. The accelerated failure time model is

\[
Z_i = X_i'\beta + e_i,
\]

where \(Z_i = \log(Y_i)\), \(\beta\) is an unknown regression parameter vector, and \(e_i\) is the error term. Suppose that \(\{e_i, i = 1, \ldots, N\}\) are independent and identically distributed and their underlying distribution is unknown.

Estimation and inference of the regression parameters are based on the estimating functions given by

\[
U(\beta) = N^{-2} \sum_{i=1}^{N} \Delta_i \omega(e_i) \left\{ X_i - \frac{\sum_{j=1}^{N} X_j I(e_i \geq e_j)}{\sum_{j=1}^{N} I(e_i \geq e_j)} \right\},
\]

where \(\omega(e_i)\) is a weight function and \(e_i = \log(Y_i) - X_i'\beta_t\), where \(\beta_t\) is the true value of \(\beta\). Let \(\omega(e_i) = 1\) and \(\omega(e_i) = \sum_{j=1}^{N} I(e_i \geq e_j); U(\beta)\) correspond to the log-rank and Gehan
statistics, respectively. The estimating functions $U(\beta)$ are step functions and discontinuous in the regression parameters, which makes it difficult to find consistent estimators and their asymptotic variance and covariance matrices. Much progress has been made to overcome these difficulties (Brown & Wang, 2006; Heller, 2007; Jin et al., 2003; Lee et al., 1993), and the function lss (lss package) can be used to obtain various statistics from an AFT model.

```r
> library(lss)
> UNA$status<- 1-(UNA$OPrem=="<")
> aftfit<- lss(cbind(log(OP), status) ~ log(Flow), data=UNA, gehanonly=FALSE, cov=TRUE)
> print(aftfit)
```

Jin et al. (2006b) extended marginal accelerated failure time models to multivariate censored data. Their method, which is based on an independence “working” model, may ignore the within-site correlations in obtaining parameter estimates, while taking account of the correlation in calculating the standard errors. More efficient estimators with similar computational complexity were developed for multivariate censored data analysis, when measurements from the same site exhibit strong temporal correlations (Fu & Wang, 2011).

5. Trend detection

In recent years, concentrations of various water quality parameters have been collected. Tests for trends specific to various water quality parameters have been of keen interest in environmental science (Helsel, 1992). A number of methods have been proposed to detect and assess changes in water quality. In this section, a variety of approaches will be introduced and their strengths and weaknesses investigated. The exogenous variable effects and serial dependence will be considered when testing water quality trends.

5.1 Parametric methods

Under the normality of residuals and constant variance assumptions, simple/multiple linear regressions are preferable for detecting trends of water quality.

5.1.1 Simple linear regression

Let $Y$ be the random variable of interest in a trend test, such as concentrations of water quality parameters. $T$ denotes time (often expressed in years). If $Y$ is linear over time $T$, the linear simple regression of $Y$ on $T$ is a test for trend.

$$Y = \beta_0 + \beta_1 T + \epsilon,$$

where $\beta_1$ is the rate of change in $Y$. The null hypothesis for testing the trend of $y$ can be stated as a test for $\beta_1 = 0$. The Wald type statistic (t-statistic) can be used. If the null hypothesis is rejected, it indicates that there is a linear trend in $Y$ over time. If $Y$ is not linear over time $T$, some transformation of $Y$, such as a log transformation, may be necessary. An example using a linear regression to detect the trend of total phosphorus concentrations at Station 1 is presented in Fig. 9. The results indicate that the trend of total phosphorus is not significant.

5.1.2 Multiple regression

Most concentrations of water quality parameters have strong seasonal patterns (see Fig. 10). They are influenced by the changes in biological activity, both natural and managed
activities such as agriculture (Helsel, 1992; Hirsch et al., 1991). Therefore, it is important to consider seasonal effects when evaluating changes in water quality data. In parametric procedures, multiple regression with periodic functions can be used to describe seasonal variation. Consider the following simple case,

$$Y = \beta_0 + \beta_1 T + \beta_2 \cos(2\pi T) + \beta_3 \sin(2\pi T) + \epsilon,$$  

(11)

where $T$ is expressed in years and $\beta_1$ indicates the change rate of $Y$. Terms $\sin(2\pi T)$ and $\cos(2\pi T)$ capture the annual cycle and account for seasonality. Residuals $\epsilon$ must follow a normal distribution (or approximately normal). The trend test can be constructed by testing $\beta_1 = 0$.

If residuals still show a seasonal pattern (see Fig. 11), additional periodic functions should be included in model (11) to remove the seasonal variation. A general multiple linear regression is given by

$$Y = \beta_0 + \beta_1 T + \sum_{k=0}^{K} [\beta_{2k+1} \cos(2\pi k T) + \beta_{2k+2} \sin(2\pi k T)] + \epsilon.$$  

(12)

The cases of $K = 0$ and $K = 1$ correspond to model (10) and (11). If $K = 2$, a period of 1/2 year is then also included in model (12). Fig. 11 shows that the residuals of the linear regression in Subsection 5.1.1 represent a seasonal pattern, therefore periodic functions should be included in the model.

When $Y$ or some transformation of $Y$ is linear with time $T$, and residuals follow a normal distribution with a constant variance, the parametric regression is optimal. However, the
distribution of water quality data is usually highly skewed, in particular, data related to discharge, as well as biological indicators (biomass, chlorophyll) (Helsel, 1992; Hirsch & Slack,
1984). The test that depends on the normality assumption may be inappropriate. The following subsection introduces several nonparametric methods that do not require the normality assumption.

5.2 Nonparametric methods

Water quality data usually have the following characteristics: nonnormal data, missing values, values below detection limits, and serial dependence. The nonparametric methods are robust and can handle these problems easily.

5.2.1 Mann-Kendall test

Mann (1945) and Kendall (1975) proposed a nonparametric test for randomness against trend. According to Mann (1945), the null hypothesis $H_0$ states that $(x_1, \ldots, x_n)$ are a sample of $n$ independent and identically distributed random variables. The alternative hypothesis $H_1$ of a two-sided test is that the distributions of $x_k$ and $x_j$ are not identical for all $k, j \leq n$, and $k \neq j$.

The test statistic $S$ is defined as

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \text{sgn}(x_j - x_k),$$

where

$$\text{sgn}(\theta) = \begin{cases} 
1 & \text{if } \theta > 0 \\
0 & \text{if } \theta = 0 \\
-1 & \text{if } \theta < 0.
\end{cases}$$

Under the null hypothesis, Mann (1945) and Kendall (1975) obtained the mean and variance of $S$.

$$E(S) = 0,$$

$$\text{var}(S) = [n(n - 1)(2n - 5) - \sum_t t(t - 1)(2t - 5)] / 18,$$

where $t$ is the extent of any given tie (number of $x$s involved in a given tie) and $\sum_t$ denotes the summation over all ties.

Both Mann (1945) and Kendall (1975) derived the exact distribution of $S$ for $n \leq 10$; proved that the distribution of $S$ is normal as $n \to \infty$; and further showed that even for $n = 10$, the normal approximate is excellent if one calculates the standard normal variate $Z$ by

$$Z = \begin{cases} 
\frac{S-1}{\text{var}(S)^{1/2}} & \text{if } S > 0 \\
0 & \text{if } S = 0 \\
\frac{S+1}{\text{var}(S)^{1/2}} & \text{if } S < 0.
\end{cases}$$

Hence, in a two-sided test for trend, the $H_0$ should be rejected if $|Z| \geq z_{\alpha/2}$, where $\Phi(z_{\alpha/2}) = 1 - \alpha/2$, $\Phi(\cdot)$ is the standard normal c.d.f. and $\alpha$ is the significance level for the test. A positive value of $S$ indicates an “upward” trend, and a negative value of $S$ presents a “downward” trend. For an example from Station 21 at Susquehanna River basin (Fig. 10), the statistic
\[ S = -90, \text{ the var}(S) = 1096.67 \text{ under the null hypothesis and the } p \text{ value is 0.0072, which indicates a downward trend in the concentration of total phosphorus at Station 21.} \]

\[ > \text{library(Kendall)} \]
\[ > \text{TP<- ts(CONY$TP, frequency=1, start=1990)} \]
\[ > \text{mk<- MannKendall(TP)} \]
\[ > \text{summary(mk)} \]

The seasonality is a common phenomenon, which indicates that the distributions differ for different times of year. The Mann-Kendall test therefore is sensitive to seasonality. \cite{Hirsch1982} developed a modified Mann-Kendall test to detect the trend of data with seasonality.

### 5.2.2 The seasonal Kendall test

\cite{Hirsch1982} presented a modified Mann-Kendall test that detects trends in time series with seasonal variation and called as a seasonal Kendall test. Let \( X = (X_1, X_2, \cdots, X_m) \) and \( X_i = (x_{i1}, x_{i2}, \cdots, x_{in_i}) \), where \( X \) is the entire sample consisting of \( m \) subsamples \( X_i \), and \( m \) is the number of seasons. Each subsample \( X_i \) contains \( n_i \) annual values. The null hypothesis \( H_0 \) is that \( X \) is a sample of independent random variables \( (x_{ij}) \), and that \( X_i \) is a subsample of independent and identically distributed random variables for \( i = 1, \cdots, m \). The alternative hypothesis \( H_1 \) is that the subsample is not distributed identically. The test statistic proposed by \cite{Hirsch1982} is given as follows. For month \( i \),

\[ S_i = \sum_{k=1}^{n_i-1} \sum_{j=k+1}^{n_i} \text{sgn}(x_{ij} - x_{ik}). \]  \hspace{1cm} (13)

Under the null hypothesis, \( S_i \) is a Mann-Kendall test statistic and

\[ E(S_i) = 0, \]

\[ \text{var}(S_i) = \left[ n_i(n_i - 1)(2n_i - 5) - \sum_{t_i} t_i(t_i - 1)(2t_i - 5) \right]/18. \]

The distribution of \( S_i \) is normal as \( n_i \to \infty \) \((t_i \text{ is the extension of a given tie in month } i)\). Define the seasonal Kendall statistic

\[ S^* = \sum_{i=1}^{m} S_{i}, \]  \hspace{1cm} (14)

and its expectation

\[ E(S^*) = \sum_{i=1}^{m} E(S_i) = 0, \]

and variance

\[ \text{var}(S^*) = \sum_{i=1}^{m} \text{var}(S_i) + \sum_{i=1}^{m} \sum_{j \neq i} \text{cov}(S_i, S_j). \]  \hspace{1cm} (15)
Under the null hypothesis, $S_i$ and $S_j$ ($j \neq i$) are independent, therefore

$$\text{var}(S^*) = \frac{\sum_{i=1}^{m} [n_i(n_i - 1)(2n_i - 5) - \sum t_i(t_i - 1)(2t_i - 5)]}{18}.$$  

The standard normal variate $Z^*$ is defined as

$$Z^* = \begin{cases} 
\frac{S^* - 1}{\text{var}(S^*)^{1/2}} & \text{if } S^* > 0 \\
0 & \text{if } S^* = 0 \\
\frac{S^* + 1}{\text{var}(S^*)^{1/2}} & \text{if } S^* < 0.
\end{cases}$$

The approximation is adequate for $n_i = 3$ and $m = 12$ for all $i$ (Hirsch et al., 1982). For the example from Station 21 at Susquehanna River basin (Fig. 10), the statistic $S^* = -360$, the $\text{var}(S) = 10779.67$ under the null hypothesis, and the $p$ value is 0.0005, which indicates a downward trend in the concentration of total phosphorus at Station 21.

A limitation of the seasonal Kendall test is one observation per month. If there are multiple observations in each of the months, Hirsch et al. (1982) suggested using the medians of the multiple observations in the seasonal Kendall test. Another limitation is that the seasonal Kendall test is not robust against serial dependence. When serial dependence exists, $\text{cov}(S_i, S_j)$ in Equation (15) does not equal zero. Hirsch & Slack (1984) provided a modification of the seasonal Kendall test which is robust against serial dependence, except when the data have very strong long-term persistence or when the sample sizes are small. More details can be found in Hirsch & Slack (1984) and Letternmatier (1988). In addition to detecting the trend, the magnitude of such a trend may also be desirable. In model (10), an estimate of $\beta_1$ can be used to estimate the trend. For a seasonal Kendall test, calculate $d_{ijk} = (X_{ij} - X_{ik}) / (j - k)$ for all pairs $(X_{ik}, X_{ij})$ and $(k < j)$. Hirsch et al. (1982) proposed using the median of $d_{ijk}$ as an estimator of the slope, which is robust against extreme values.

### 5.2.3 Sen’s T test

Farrel (1980) proposed an aligned-rank test for detecting trends, which is distribution free and not affected by seasonal fluctuations (Van Belle & Hughes, 1984; Yu et al., 1993). Let $x_{ij}$ be the measurement in the $i$th month of the $j$th year at a sampling station, and $i = 1, \ldots, m, j = 1, \ldots, n$. Let $R_{ij}$ be the rank of $(x_{ij} - x_{i+})$ among the $mn$ values of differences, where $x_{i+} = \sum_{j=1}^{n} x_{ij}$. If ties occur, the average of the ranks is taken as the rank of each tie. The statistic is

$$T = \left\{ \frac{12m^2}{n(n + 1) \sum_{i,j} (R_{ij} - R_{i+})^2} \right\}^{1/2} \left\{ \sum_{i=1}^{n} \frac{(i - \frac{n + 1}{2})}{2} (R_{+j} - \frac{nm + 1}{2}) \right\},$$

where $R_{i+} = \sum_j R_{ij} / n$ and $R_{+j} = \sum_i R_{ij} / m$. Under the null hypothesis of no trend, the distribution of $T$ tends to the standard normal distribution. Simulation results indicated that the normal approximation for the statistic $T$ was reasonable even for a small sample (Van Belle & Hughes, 1984).
The three nonparametric methods for detecting trends mentioned above have practically the same power at a statistical significance level of 0.05 (Yu et al., 1993). It is worth noting that there may exist water quality parameters which exhibit strong evidence of a download trend in some months and then exhibit strong evidence of an upload trend (step trend) (Helsel, 1992; Hirsch et al., 1991). The methods described above all assume a single trend across all seasons, provide a summary statistic for the entire record (monotonic trend), and do not indicate when there are trends in opposing directions in different months. Van Belle & Hughes (1984) developed a statistic for testing homogeneity of trends. The statistic is

$$\chi^2_{\text{homogeneous}} = \chi^2_{\text{total}} - \sum_{i=1}^{m} Z_i^2 - mZ^2,$$

where $$Z_i = S_i / \sqrt{\text{var}(S_i)}$$, $$S_i$$ is the Mann-Kendall statistic in Equation (13), and $$Z = \sum_{i=1}^{m} Z_i / m$$. Under the null hypothesis that the seasons are homogeneous with respect to trend, $$\chi^2_{\text{homogeneous}}$$ approximates the chi-square distribution with $$m - 1$$ degree of freedom. If $$\chi^2_{\text{homogeneous}}$$ exceeds the critical value, it indicates that there are different trends among different seasons. In that case, the three nonparametric methods are not meaningful, and the Mann-Kendall statistic can be used to test the trend for each individual season.

### 5.3 Adjusting covariate effects on trend tests

Several variables ($$X$$) other than time trend usually have considerable influence on water quality parameters ($$Y$$) (see Fig. 12). These variables are natural and random phenomena such as rainfall, temperature, and stream flow. To detect the trend of water quality parameters with time ($$T$$), these variable effects on water quality parameters need to be removed. The removal process includes modeling and explaining variable effects with regression methods and the LOWESS method (Helsel, 1992).

```r
> xyplot(log(TP) ~ log(Flow) | Year, col.line = 2, type = c("p", "r"), data = UNA, xlab = "Log values of flow", ylab = "Log values of total phosphorus concentrations")
```

#### 5.3.1 Parametric methods

Consider a linear regression of $$Y$$ versus time $$T$$ and one or more covariates $$X$$,

$$Y = \beta_0 + \beta_1 T + \beta_2 X + \varepsilon.$$

For the trend test, the null hypothesis is $$\beta_1 = 0$$. The t-statistic can be used for the trend test. This model simultaneously explains the covariate effect and detects the trend with time. If the covariate changes with time, the following regression can be considered.

$$Y = \beta_0 + \beta_1 T + \beta_2 X + \beta_3 T \ast X + \varepsilon,$$

where $$T \ast X$$ is the interactive term. For regression models, the relationship (linear function) between $$Y$$ and $$X$$ must be checked. Residuals should have no outliers and a constant covariance. The functions in R for testing these assumptions can be found in Subsection 5.4. According to the previous analysis, we use the following multiple linear regression to detect the trend of total phosphorus at Station 1. This model adjusts the flow effect and also captures the annual cycle.

$$\ln(C) = 2.25 - 0.74 \text{Time} - 0.43 \sin(2\pi\text{Time}) + 0.22 \cos(2\pi\text{Time}) - 1.81 \ln(\text{Flow}) + 0.096 \text{Time} \ast \ln(\text{Flow}) + 0.15 \ln(\text{Flow})^2$$
Fig. 12. Log values of total phosphorus concentration (C) versus log values of flow (F)

The results indicate an annual cycle and flow effect exist (p<0.05). After adjusting exogenous variables effects, the concentration of total phosphorus significantly decreases (p = 0.02).

5.3.2 Semi/nonparametric methods

Hirsch & Slack (1984) provided an adjusted seasonal Kendall test and proposed the following mixture procedure to test trends: (a) Use a regression model $Y = f(\beta X) + \epsilon$ to find the relationship between the concentration and covariates, where $f(\cdot)$ is a certain function of covariate $X$; (b) If there exists a significant relationship, compute the adjusted concentration $Y_{ik} - \hat{Y}_{ik}$, where $\hat{Y}_{ik} = f(\hat{\beta} X)$ is the estimated concentration of $Y_{ik}$; (c) Then apply the seasonal Kendall test for trend and slope estimator to the time series of $Y_{ik} - \hat{Y}_{ik}$.

The nonparametric LOWESS method (Cleveland, 1979; Helsel, 1992) can be used to remove a covariate effect without previously assuming the form of the relationship between $Y$ and $X$. It is solely determined by the dataset and therefore it is robust to the distribution of the data pattern. The function lowess in the statistical software R can be used to obtain the fitted values $\hat{Y}$ of $Y$. The seasonal Kendall statistic (14) is calculated from $Y - \hat{Y}$ and $T$ data pairs.

The parametric regression method can simultaneously check the covariate effect and detect the trend. When the linearity and normality assumptions are met, the parametric regression method outperforms for detecting and estimating the magnitude of trends. Otherwise, the LOWESS method is a desirable alternative. To examine the trend of a water quality parameter, the covariate and seasonal effects need to be removed. According to the real datasets, choose a reasonable statistical approach to test for trends. Various methods for trend tests are given in Table 1. For water quality data with detection limits, parametric Tobit regression (9) can be used. When a fixed detection limit exists, all the data below the fixed detection limit can be...
considered to be tied with each other. The nonparametric procedures such as Mann-Kendall, and the seasonal Kendall statistics can be used directly. If multiple detection limits exist, censor the data at the highest detection limit and then use an appropriate method to test the trend. Some information is certainly lost by making this change.

<table>
<thead>
<tr>
<th></th>
<th>No exogenous covariate (X) effects</th>
<th>Seasonality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parametric</td>
<td>Regression of Y on T</td>
<td>Regression of Y on T and Seasonal terms</td>
</tr>
<tr>
<td>Nonparametric</td>
<td>M-K test</td>
<td>S-K test</td>
</tr>
<tr>
<td>Mixed</td>
<td>S-K test on residuals from regression of Y on X</td>
<td>S-K test on residuals from regression of Y on X</td>
</tr>
<tr>
<td></td>
<td>Exogenous covariate (X) effects exist</td>
<td>Seasonality</td>
</tr>
<tr>
<td>Parametric</td>
<td>Regression of Y on (T, X)</td>
<td>Regression of Y on (T, X, S)</td>
</tr>
<tr>
<td>Nonparametric</td>
<td>M-K of residuals from regression of Y on (T, X)</td>
<td>S-K of residuals from lowess of Y on X</td>
</tr>
<tr>
<td>Mixed</td>
<td>M-K of residuals from regression of Y on (T, X)</td>
<td>S-K of residuals from regression of Y on (T, X, S)</td>
</tr>
</tbody>
</table>

Table 1. Classification of various types of tests for monotonic trend. M-K indicates Mann-Kendall test, S-K indicates Seasonal Kendall test, and S denotes seasonal terms.

5.4 Computational implementation for linear regression models using R

In this subsection, we will show how to use the statistical software R to fit, evaluate and modify a linear regression model. More details can be seen in Adler (2009), Crawley (2007), and Venables & Ripley (2002).

A linear regression model is one of the most classic and popular methods in statistical practice. It is a very important tool for the statistical analysis of water quality data. It assumes that there is a linear relationship between a response variable (continuous) and some covariate variables. To fit a linear regression model to a dataset, the primary function is `lm`. We begin with the dataset mentioned in Section 2 to show how to fit a linear model in R. R codes for fitting the dataset are as follows.

```r
> con.lm <- lm(log(TP) ~ log(Flow) + pH, data = UNA)
```

To print a simple display of the fitted information, use the `print` function:

```r
> print(con.lm)
```

To obtain conventional regression analysis results, use the `summary` function:

```r
> summary(con.lm)
```

To extract the regression coefficients, use the `coef` or `coefficients` function:

```r
> coef(con.lm)
```

To obtain the variance-covariance matrix for the model fitted above, use the `vcov` or `Var` function:

```r
> vcov(con.lm)
```

To calculate the confidence intervals for the coefficients in the fitted model, use the `confint` function:

```r
> confint(con.lm, level = 0.95)
```

To get the residuals, use the `resid` or `residuals` function:

```r
> resid(con.lm)
```

To obtain the fitted values, use the `fitted` or `fitted.values` function:

```r
> fitted(con.lm)
```

To return the deviance of the fitted model, use the `deviance` function:

```r
> deviance(con.lm)
```

To refit the model, it is better to use the `update` function, which can save some typing. For
example, a slightly different model is used to fit the data above, which considers an extra covariate “Temp” besides “Flow” and “pH”.

```r
> con.lm2 <- update(con.lm, . ~ . + Temp)
```

To compare models `con.lm` and `con.lm2` which are used to fit the same dataset, use the `anova` function:

```r
> anova(con.lm, con.lm2)
```

The main arguments to the function `lm` are:

```r
> lm(formula, data, weights, subset, na.action)
```

where `formula` is the model formula that specifies the form of the model to fit; `data` is an optional data frame containing the variables in the model; `weights` is a positive numeric vector containing weights to be used in the fitting process; `subset` is an optional vector specifying a subset of observations to be used in the fitting process; and `na.action` is a function which indicates how to handle missing values contained in the data.

The least-squares method performs well when the following key assumptions are satisfied: (1) There is a linear relationship between any pair of covariate variables (linearity); (2) The error terms are normally distributed (normality) with a constant variance (homoscedasticity); (3) The error terms are not correlated with each other (autocorrelation). However, because these assumptions may not be met in water quality data, linear regression is therefore not always appropriate. The test functions can be used to check these assumptions in R. The function `ncv.test` in the `car` package can be used to test the homoscedasticity. The function `durbin.watson` (car package) is used to test autocorrelation in a linear regression model. Diagnostic plots can also provide checks for homoscedasticity, normality, and influential observations (see Fig. 13), which can be obtained using the function `plot(con.lm)`.

![Residuals vs Fitted](image1)
![Scale-Location](image2)
![Normal Q-Q](image3)
![Residuals vs Leverage](image4)

Fig. 13. Diagnostic plots for a linear regression model
6. Conclusions

Statistical methods are important in water quality analysis because much of what is known about water quality comes from numerical datasets. In this chapter, various statistical methods for analyzing water quality data have been introduced. Three typical graphs, boxplots, Q-Q plots, and scatter plots, which contain appropriate summarized information about datasets, are used to provide insight for analysts into datasets. A variety of classic water quality indices are applied to give a global assessment of water quality. Weighted water quality indices are relatively subjective; unweighted water quality indices and Harkins’ water quality index are more objective. Other more advanced methods can be found in Raican et al. (2011) and Qian et al. (2007). To handle water quality data with detection limits, simple substitution methods as well as parametric and nonparametric approaches are investigated. Substitution methods are simple but possibly biased. Nonparametric methods which do not require the distributional assumption are robust and efficient (Helsel, 2005). Several popular methods, such as Mann-Kendall, the seasonal Kendall test, and multiple regression methods, are provided to detect and assess changes of various water quality parameters (Helsel, 1992). Meanwhile, nonlinear trends, serial dependence, covariate effects, and irregular measurement patterns need to be considered (Abaurrea et al., 2011; Morton & Henderson, 2008). Computational implementation using R for linear regression models is introduced. Examples using a real dataset are given to illustrate some very useful R functions.

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8. References


The book attempts to cover the main fields of water quality issues presenting case studies in various countries concerning the physicochemical characteristics of surface and groundwaters and possible pollution sources as well as methods and tools for the evaluation of water quality status. This book is divided into two sections: Statistical Analysis of Water Quality Data; Water Quality Monitoring Studies.

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