ISEIS

Journal of Environmental Informatics 16(1) 35-42 (2010)

Journal of Environmental Informatics

www.iseis.org/jei

A Robust Statistical Analysis Approach for Pollutant Loadings in Urban Rivers

J. Ping[2], Y. Chen[2], B. Chen[1,2,*], and K. Howboldt[2]

[1]*Research Academy of Energy and Environmental Studies, North China Electric Power University, Beijing, 102206, China*
[2]*Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5, Canada*

Received 24 May 2010; revised 30 July 2010; accepted 28 August 2010; published online 10 September 2010

ABSTRACT. With rapid urbanization and economic development, anthropogenic activities have brought stressors on urban water resources. This study aims to develop a robust statistical approach for analyzing pollutant loadings in urban rivers to support water management decisions and practices. In order to test the developed approach and demonstrate its feasibility and robustness, a case study was conducted in two urban rivers in eastern Canada. The results indicated that the changes of lead (Pb) concentration in both rivers were not statistically significant among different sites over years; the upward or downward monotonic trend of Pb concentration in each site was also not significant; no significant step trend was found by using Mann-Whitney test; interval analysis verified that the Pb concentration in 2009 and 2010 met the local surface water quality guideline; the self-purification capacities of the two rivers were much limited to reduce the concentrations of Pb in the water; Moreover, the adaptation of the probability plotting method shows the robustness and effectiveness in investigating multiply censored water quality datasets rather than simple substitution procedures commonly used in practice.

Keywords: pollutant loadings, two-way ANOVA analysis, trend analysis, interval analysis, bootstrapping method, multiply censored data analysis

1. Introduction

Fresh water is fundamental to human development as well as ecosystem function. With accelerating urbanization and economic development, anthropogenic activities especially under inappropriate management impact urban water quality and volume (BRAGA, 2001). A great number of studies have been conducted to assess water quality compliance with regulatory guidelines as well as the impact of contaminants on water bodies (Buelna and Riffat, 2007; Warner et al., 2007; Chen, 2008; Montgomery and Eames, 2008; Müller et al., 2008; Awuah et al., 2009; Mkandawire and Banda, 2009; Ipeaiyeda and Onianwa, 2009; Qin et al., 2009; Li et al., 2010; Pedusaar et al., 2010).

Although comprehensive with respect to water quality assessment, most previous studies usually used their own data, and thereby eliminating much of the uncertainty in sampling; otherwise, the influence of uncertainties associated with the factors affecting sampling results should be statistically evaluated when using other researcher's data. Some key factors include timing, frequency, equipment used in field and lab, location, and environmental conditions. Given that most samples are grabbed in a specific location and time. Multiple samples are usually needed over a period of time and different locations in order to obtain an overall picture of the water body. However, over this time period, the equipment used may change, sample locations may vary, and/or sampling teams may be different. To account for the variations, basic statistical methods (average, minimum/maximum, standard deviation, etc.) have been employed previously to analyze sampling results, which may lead to loss of valuable information (Ahmed et al., 2000; D'Vera, 2005; Montgomeryand and Eames, 2008; Jin et al., 2009; Wiatkowski and Paul, 2009; Munabi et al., 2009). Further, different analytical instruments used to measure the same contaminant may bias the results due to different detection limits. Readings may be simply ignored or replaced in reportting, (Buelna and Riffat, 2007; Town of Markham, 2009; Town of Newmarket, 2009). The influence of sampling/measurement methods and instruments, environmenttal conditions, and even sampler's behaviours on the quality of results are seldom studied. For example, many studies failed to take into account the influence of various sampling seasons, different samplers and measurement methods to the sample results (Canter and Maness, 1995; Ahmed et al., 2000; Buelna and Riffat, 2007; Awuah et al., 2009; Mkandawire and Banda, 2009).

To address the above challenges, more systematic and robust statistical approaches are desired for supporting water management. This study aims to develop an integrated water quality analysis approach, which will be able to a) examine the influences caused by the variations of both site conditions and

* Corresponding author. Tel.: +1 709 7378958; fax: +1 709 7374042.
E-mail address: bchen@mun.ca (B. Chen).

ISSN: 1726-2135 print/1684-8799 online
 doi:10.3808/jei.201000176

timing of sampling; b) determine the trend and distribution of contaminant concentrations; c) determine impacts due to variation in sampling methods and teams; d) quantify uncertainties associated with the compliance assessment; e) investigate the self-purification capacity; and f) assess the test results obtained from the equipment with different detection limits.

2. Methodologies

Figure 1 shows the framework of the developed approach. The development will be based on a) two-way ANOVA analysis method to determine the potential trend of contaminant concentrations associated with the change of time and space; b) trend analysis to investigate the trend of contaminants during the sampling period and the step trend caused by sampling methods and teams as well as sample analysis facilities; c) confidence interval in the data analysis to test its compliance with urban water quality guideline; d) a balanced ANOVA to assess the difference on self-purification capability of each river; e) probability plotting method to assess collected water quality data with under different detection limitations.

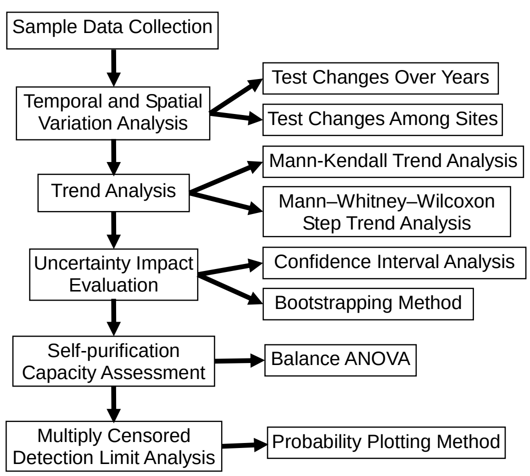

Figure 1. Framework of robust statistical analysis approach for pollutant loadings in urban rivers.

2.1. Temporal and Spatial Variation Analysis

Water quality data varies with time and location, particularly in rivers. The first step is to determine if there are significant changes in contaminant concentrations over a given time period or among different sites. A two-way analysis of variance (ANOVA) was employed in this study. In statistics, analysis of variance (ANOVA) is a collection of statistical models, and their associated procedures, in which the observed variance is partitioned into components due to different sources of variation. One-way ANOVA measures significant effects of one factor only, while two-way ANOVA measure the effects of two factors simultaneously. Two-way ANOVA can therefore assess both time and site in the same test, and determine if there is an interaction between the parameters. A two-way test generates three *p*-values, one for each parameter independently, and one measuring the interaction between the two parameters.

2.2. Trend Analysis

Trend analysis looks for changes in environmental parameters over time or in space. Mann-Kendall (MK) trend analysis (McLeod et al., 1990) determines whether there is a monotonic (single-direction) trend over time. It is a nonparametric test, determining trend regardless of whether that trend is linear or whether data follow a normal distribution. On the other hand, significant changes might exist in the contaminant concentration as a result of different samplers, various sampling methods, as well as climatic conditions. To account for this, the Mann–Whitney–Wilcoxon (MWW) test was used on conjunction with MK analysis, to determine if the two independent samples of observations have equally large values. The MWW is virtually identical to performing an ordinary parametric two-sample t test on the data after ranking over the combined samples.

2.3. Uncertainty Impact Evaluation

The measured concentrations of contaminants vary from year to year at each site, which complicates assessment of compliance with local water quality guidelines. A confidence interval (CI) is a particular kind of interval estimate of a population parameter used to account for the variability (Smithson, 2003). Taking the water quality data analysis as an example, if the water quality regulations indicated that the 90th percentile concentration of contaminants should not exceed guidelines due to the uncertainties of environmental data, the interval analysis determines if the standard has been violated by the 90th percentile of concentrations at the 90% confidence level. Instead of estimating the parameter by a single value, an interval likely to include the parameter is given. Thus, confidence intervals are used to indicate the reliability of an estimate. How likely the interval is to contain the parameter is determined by the confidence level.

Bootstrapping is a computer-intensive, general purpose approach to statistical inference, falling within a broader class of re-sampling methods (Davison and Hinkley, 2006). It is often used as an alternative to inference based on parametric assumptions when those assumptions are in doubt, or where parametric inference is impossible or requires complicated formulas for the calculation of standard errors. Compared with other analytical methods, it is straightforward to apply the bootstrap to derive estimates of standard errors and confidence intervals for complex estimators of complex parameters of the distribution, such as percentile, proportions, odds ratio, and correlation coefficients. In the water quality analysis, bootstrapping can be incorporated into interval analysis for reflecting the uncertainties.

2.4. Self-purification Capacity Assessment

Once the contaminant is discharged into environment, it could be possibly decomposed or diluted. However, the self-purification capability of water systems varies, depending on the characteristics of the water system and type/volume of contaminant loadings. Therefore, it is essential to assess the degradation capability of each river at different sites. Two-way ANOVA is most powerful when the experiment has the same number of replicates in each group defined by the pair of parameters, which is called a "balanced design". Comparison of a certain contaminant between rivers will be made to test whether they are statistically significant or not. The results from the balanced ANOVA could indicate the levels of self-purification capacity when there are significant changes in concentrations of the contaminant.

2.5. Descriptive Multiply Censored Detection Limit Analysis

Water quality data often contain "less than" observations. Rather than the situation where only one detection limit was present, the performance of estimators for data that have multiple detection limits should be investigated. Multiple detection limits arise because of 1) improvement in analytical methods over time, resulting in a lowering of the detection limits, 2) management decisions to reduce costs by use of methods with higher detection limits, 3) combination of data from several agencies or laboratories having different reporting levels, or 4) use of differing laboratory procedures and detection limits due to differences in sample matrix characteristics. When utilized correctly, less than values frequently contain nearly as much information for estimating population moments and quantiles as would the same observations had the detection limit been below them. A probability plot is a graphical data analysis technique for determining how well the specified distribution fits the data set. Linearity in the probability plot is indicative of a good distributional fit. Probability plotting methods is used in this study due to its robustness to describe the multiply censored data. One advantage of the graphical approach over quantitative measures (e.g., Kolmogorov-Smirnov test) is that it provides an indication of how the distribution is not a good fit. This can provide guidance to a better distributional model.

3. A Case Study

The contaminant of interest in this study is Lead (Pb), which can accumulate in individual organisms and even the entire food chains. The accumulation of Pb can cause kidney damage, brain damage, disruption of nervous systems, and behavioural problems to both human and aquatic life (EPA, 2010). Along with the rapid urbanization, Pb can be added to the environment from anthropogenic activities such as industrial operations (EPA, 2010). In order to test the developed approach and demonstrate its feasibility and robustness, a case study was conducted in two urban rivers in eastern Canada.

3.1. Overview of the Study Area

To protect the confidential information of the parties involved in this study, the identifications and geographical locations of the rivers and the city are removed. In this study, Rivers A and B, located at the western outskirts of City X in eastern Canada, were selected to assess the Pb loadings in the watershed. River A, flowing across an industry zone, is the main head-water tributary of River B, which flows through a densely populated region. River B is not a drinking water resource, but is used recreationally for fishing and swimming. The water quality of River A is impacted by industrial activities midway along its path through the industrial zone. An intensive field investigation especially source identification and historic records review have been conducted. The Pb is attributed to a series of past and ongoing industrial activities including emissions from industrial processes and incineration of solid wastes, and the surface runoff from mining activities at quarry sites (Environment Canada, 2008). The source of Pb contamination of River A could possibly pose health risks to the residences living along River B, as well as to flora and fauna in the surrounding area.

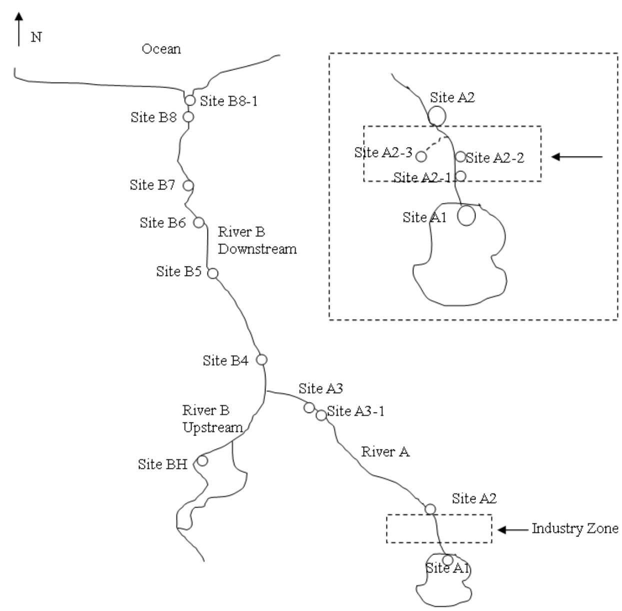

Figure 2. Locations of new 6 sites in Rivers A and B (flow direction is from south to north).

3.2. Data Acquisition

The water sampling program was carried out from 2006 to 2010 at Rivers A and B. Three sites along the River A and five sites along the River B were monitored throughout the study period (Figure 2). Among those sites, Site A1 is the headwater of A, regarded as a reference representing the natural conditions of the water system; Site A2 is located at the downstream of the industrial zone, where water quality may have been impacted by various industrial activities; Site A3 is located in the outlet of a gully around 1 km upstream from the junction of the two rivers, which represents the water quality of River A flow into River B, and can be used to assess the impact of River A to River B. The other five sites were chosen along the River B to evaluate water quality at River B. Site B4 is located near the junction point of the two rivers and it is used to reflect the loading contribution of the tributary of River B. Sites B5 ~ 7 are located in the residential area which is more vulnerable to the Pb contamination and requires more attention during pollution analysis. The results of Pb concentration of the eight sites from 2006 to 2010 are summarized in Table 1.

Table 1. Pb Concentrations (ppb) from 2006 to 2010

Sampler Site	Group 1			Group 2	
	2006	2007	2008	2009	2010
A1	0.80	0.45	0.11	0.36	0.35
A2	0.48	1.90	0.57	0.43	1.56
A3	0.17	0.62	0.17	0.44	0.26
B4	0.24	0.36	0.37	0.38	0.22
B5	0.25	0.35	0.12	0.37	0.19
B6	0.19	0.50	0.08	0.19	0.11
B7	0.36	0.47	0.16	0.81	0.70
B8	0.43	0.17	0.25	0.78	0.28

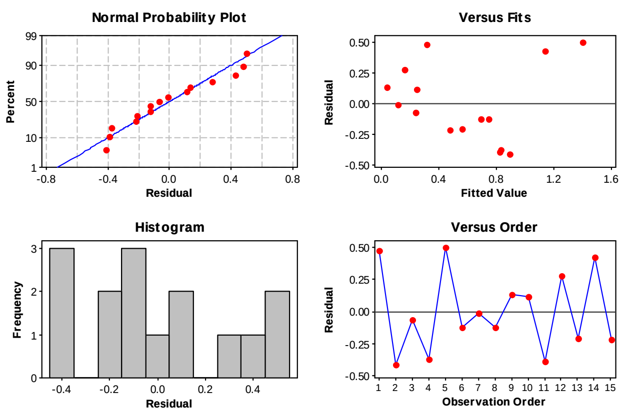

Figure 3. Residual plots for Pb concentration in River A.

4. Results and Discussion

4.1. Two-way ANOVA Analysis

In this study, Two-way ANOVA analysis will be conducted using Minitab (Version 5.1), provided by Minitab Inc. The first step is to check whether there are significant changes in Pb concentration during 5 years or among the different sites for each river, respectively. The assumptions for 2-factor ANOVA in this case are that residual are normally distributed and variances are constant at α = 5%. Since there is no replication in the data set, there is no need to consider the interactions.

The hypotheses for water quality ANOVA of River A are:
H_{01}: Pb concentrations during the years are equal;
H_{11}: Pb concentrations during the years are not equal;
H_{02}: Pb concentrations among the sites are equal; and
H_{12}: Pb concentrations among the sites are not equal.

From the results of the Two-way ANOVA Analysis for River A, the R-Sq(adj) value 33.55% is pretty low. Also, the residual plots of the original datasets (Figure 3) show funnel pattern, which means the variance are not constant, therefore the logarithm transformation of the Pb concentration is conducted for the ANOVA analysis. After logarithm transformation of the data, the R-Sq(adj) increased (i.e. 43.74%) and the residuals (Figure 4) are fairly well spread out. Assumptions (normality, constant variance and randomized residues) are satisfied for ANOVA. The results show that both p-values (i.e. 0.19 and 0.05) are greater or equal than 0.05. Therefore, it can be concluded that there is no significant changes among different sites and over the years in River A. Also the results show there is no significant interaction effect between the two factors (i.e. sampling site and time).

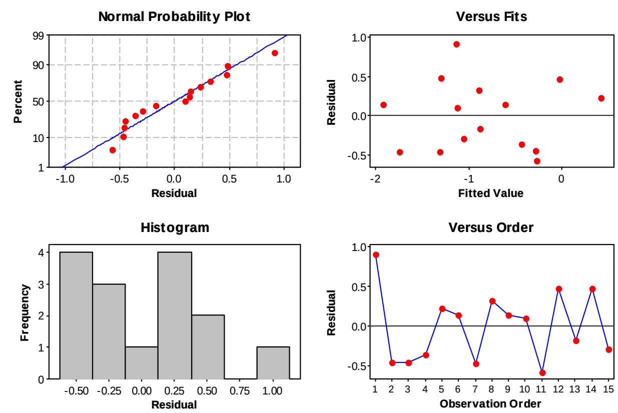

Figure 4. Residual plots for log-transformed Pb concentration in River A.

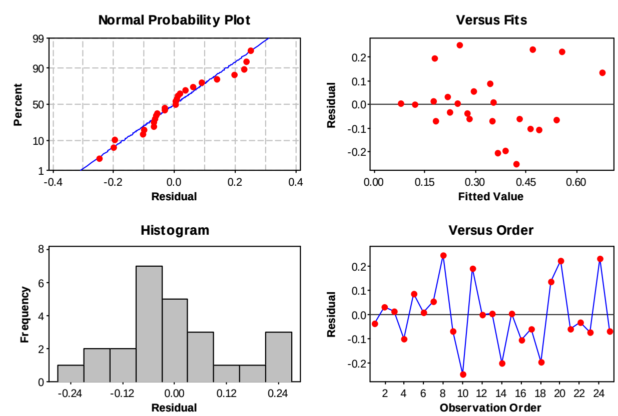

Figure 5. Residual plots for Pb concentration in River B.

The hypotheses for water quality ANOVA of River B are the same as River A. As what happened in the original data analysis of River A, the obtained R-Sq(adj) value 55.02% is very low and the residual plots (Figure 5) also show unequal variance, thus the logarithm transformation of the Pb concentration is conducted for the ANOVA again. The two-way ANOVA results after logarithm transformation of the data indicate that the R-Sq(adj) increased and the residuals (Figure 6) are fairly well spread out. Assumptions are satisfied for ANOVA. Also both p-values (i.e. 0.052 and 0.064) are greater than

0.05. It can be concluded that there is no significant changes among different sites and over years in River B. Also the results show there is no significant interaction effect between the two factors.

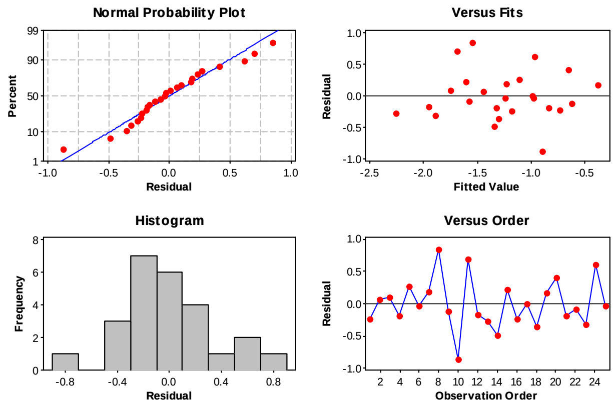

Figure 6. Residual plots for log-transformed Pb concentration in River B.

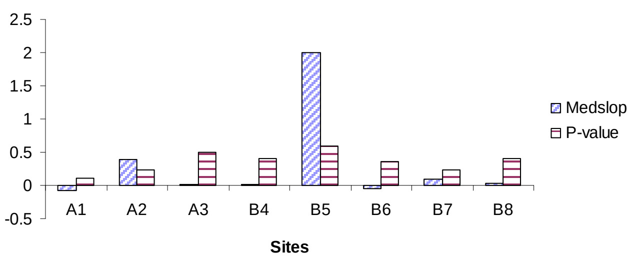

Figure 7. Summary of trend analysis by year.

4.2. Trend Analyses

4.2.1. Mann-Kendall Trend Analysis

To test whether there is any statistically significant trend of the Pb concentration at each site over the years. For n = 5 < 10, an exact test of the MK trend analysis was used. For instance, at site A1 the median of all pairwise slopes is negative, indicating a possible downward monotonic trend. However, from the Table of Quantiles (*p*-values) for Kendall's tau correlation coefficient (Kendall, 1975) n is equal to 5 and S is -6, and the *p*-value is 0.117, greater than 0.05, so the null hypothesis (H_0: The monotonic trend is not significant) cannot be rejected. Figure 7 summarized the results of trend analysis by year and indicates there is no monotonic trend of the Pb concentration at each site over the years.

4.2.2. Mann–Whitney–Wilcoxon Step Trend Test

In this study, water samples were collected by one set of researchers from 2006 to 2008, and a different set from 2009 to 2010. Changes in the Pb concentration in samples may be caused by different samplers as well as different sampling methods. Therefore, robust non-parametric method by using LOWESS residuals followed by MWW test was conducted to test the possible step trend. The results are list in Table 2. The estimated difference between the two steps is -0.045 and the 95.2% confidence interval of it is from -0.2 to 0.09, which includes zero. Also, the resulting P-value is 0.4154, greater than 0.05. All the above help conclude that there is no significant step-trend caused by different samplers as well as different sampling methods, also detected by box-plots of the data (Figure 8).

Table 2. Whitney Test and CI: Pre-2008, Post-2008

	N	Median
Pre-2008	24	0.3550
Post-2008	16	0.3650
Point estimate for ETA1-ETA2	-0.0450	
95.2 Percent CI for ETA1-ETA2	(-0.2000, 0.0900)	
W	462.0	

Test of ETA1 = ETA2 vs ETA1 not = ETA2 is significant at 0.4154;
The test is significant at 0.4150 (adjusted for ties).

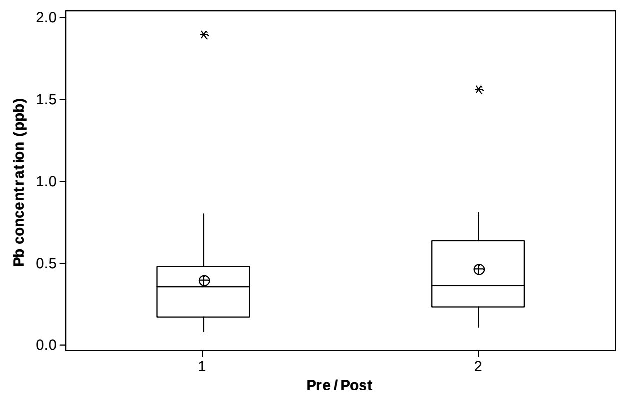

Figure 8. Boxplot of Pb level collected by different groups.

4.3. Bootstrapping-enhanced Interval Analyses

Six new sites were added in 2009 and 2010 due to their critical locations for pollution investigation (Figure 2). Site A2-1 is located in the stream close to the chemical handling facility and is at the upstream of the junction of two small tributaries. Site A2-2 was chosen at a small pond, where two tributaries meet. Site A2-3 is located at another tributary of River A. Site A3-1 is close to the inlet of a gully around 1 km upstream from the River A and River B junction. Site B8-1 was chosen at the mouth of estuary where tide occurred periodically. It is suspected the sudden change of water quality in Site B8 caused by the reflux of sea water. Site BH is located at the headwater of River B. Similar as the headwater of River A, this site is located in a boggy wetland area, surrounded by high population of trees. The water quality at this site can be used as a reference for the River B, since no human or industry an activity was found around this site.

According to CCME guidelines for the protection of aquatic life, the Pb concentration should not exceed 1 ug/L (ppb) (CCME, 1999). The measured Pb concentrations vary from year to year at each site, which complicates compliance assessment. Most of water quality regulations indicated that the 90th percentile concentration of contaminants should not exceed guidelines due to the uncertainties of environmental data (Helsel and Hirsch, 2002). Site A1 and Site BH are the headwaters of River A and River B, both of which are far away from any anthropogenic influence, so those two sites are not considered. Site B8-1 is located at the outlet of the estuary of River B to the sea and the contaminant level would be strongly affected by the sea water. Figure 9 shows the Pb concentrations at the 14 sites in 2009 and 2010.

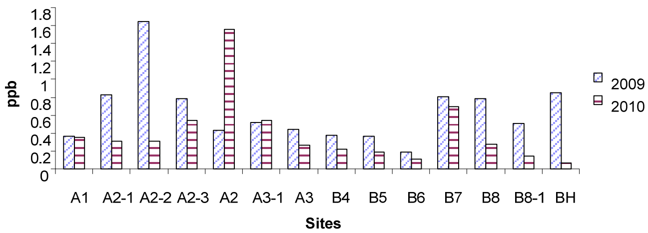

Figure 9. Pb concentration data in 2009 and 2010.

This is a one-side confidence interval analysis aiming at finding the lower limit of 90% confidence interval (α = 0.10 or $\alpha/2 = 0.05$), then comparing the lower confidence limit with the given standard = 1 ppb. The descriptive statistics of the data sets for each year are generated by Minitab and summarized in Table 3, including the number of data points (N), mean value of data, minimum and maximum of the data points, square error of the mean (SE Mean), standard deviation (StDev), variance, 25% quartile and 75% quartile (Q1 and Q3), as well as the skewness of the set of data. Bootstrapping method is applied to calculate the 90% low Confidence Intervals of both year. To conduct the re-sampling method, the two data sets are ranked from low to high. For detailed bootstrapping analysis of both years. It was found from the results that the 90% low confidence intervals of both year are less than 1 ppb (standard), the Pb concentration in 2010 is even less than that of 2009.

Table 3. Descriptive Statistics of Pb concentrations (ppb)

Variable	N	Mean	SE Mean	StDev
2009	12	0.640	0.109	0.377
2010	12	0.431	0.115	0.397
Variable	Minimum	Median	Maximum	Skewness
2009	0.193	0.516	1.642	1.78
2010	0.110	0.292	1.559	2.37

4.4. Balanced ANOVA Analysis

Since it is essential to assess the degradation capability of each river at different sites, the following step is to evaluate the self-purification due to dilution and natural degradation capacity of the water body. Balanced ANOVA Analysis is applied to test whether the Pb level in River 2 is significantly decreased than that of the River 1. Table 4 lists the data for ANOVA Analysis. From the residual plots for Pb data (Figure 10), all assumptions are satisfied. All p-values are greater than 0.05. Hence, there is no difference between rivers and also no differences among the sites within the chosen river. In other word, the Pb purification capability of each river is poor.

Table 4. Data for Balanced ANOVA Analysis (Pb concentration: ppb)

River A			River B		
	2009	2010		2009	2010
A2-1	0.83	0.30	B4	0.38	0.22
A2-2	1.64	0.31	B5	0.37	0.19
A2-3	0.78	0.54	B6	0.19	0.11
A2	0.43	1.56	B7	0.81	0.70
A3	0.44	0.26	B8	0.78	0.28

Table 5. Multiply Censored Water Quality Data in 2006 (Pb concentration: ppb)

Site	June	July	August	September
A1	0.80	< 0.56	0.54	0.70
A2	0.48	< 0.61	0.69	1.76
A3	0.17	< 0.56	0.28	0.57
B4	0.24	1.11	0.14	0.15
B5	0.25	< 0.61	0.19	< 0.15
B6	0.19	< 0.53	0.25	0.24
B7	0.36	< 0.70	< 0.12	< 0.12
B8	0.43	< 0.61	0.29	0.50

Table 6. Calculated A_i and B_i Value (Pb concentration: ppb)

	A_i		B_i	
N = 32	$A_6 = 4$	i > 0.7	$B_1 = 2$	< 0.12
m = 6	$A_5 = 1$	0.61 < i < 0.70	$B_2 = 4$	< 0.15
	$A_4 = 1$	0.56 < i < 0.61	$B_3 = 19$	< 0.53
	$A_3 = 1$	0.53 < i < 0.56	$B_4 = 22$	< 0.56
	$A_2 = 14$	0.15 < i < 0.53	$B_5 = 26$	< 0.61
	$A_1 = 1$	0.12 < i < 0.15	$B_6 = 28$	< 0.7

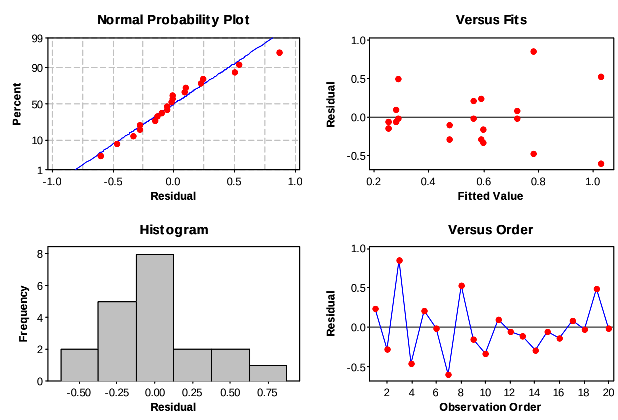

Figure 10. Residual plots for Pb data.

4.5. Probability Plotting of Multiply Censored Water Quality Data

Previously, procedures were evaluated when no detection limit was present. Actually, in 2006, more data were collected in other months but with multiple detection limits. The data used before are just part of them but consistent with the same period as the data collected in other years. The database for 2006 is summarized in Table 5. Hirsch and Stedinger (1987) define a variable A_i as the number of uncensored observations above the jth threshold (here the jth detection limit) and below the next highest threshold. They also define B_i as the number of observations, censored and uncensored, below the jth threshold. The data set in this case has n = 32 observations and m = 6 detection limits. The calculated A_i, and B_i are listed in Table 6. In general, the probability of exceeding the jth threshold $P_{e,j}$ is given as:

$$P_{e,j} = P_{e,j+1} + [A_j/(A_j + B_j)](1 - P_{e,j+1}) \quad (1)$$

which is solved iteratively for $j = m, m\text{-}1, \ldots 2, 1$. By convention, $P_{e,m+1} = 0$.

Table 7. Plotting Positions for Pb Concentrations (ppb) in 2006

Recorded uncensored observations	Plotting position	Recorded censored observations	Plotting position
0.14	0.153	< 0.12	0.045
0.15	0.209	< 0.12	0.091
0.17	0.249	< 0.15	0.085
0.19	0.289	< 0.53	0.383
0.19	0.329	< 0.56	0.269
0.24	0.369	< 0.56	0.537
0.24	0.408	< 0.61	0.281
0.25	0.448	< 0.61	0.562
0.25	0.488	< 0.61	0.842
0.28	0.528	< 0.7	0.438
0.29	0.567		
0.36	0.607		
0.43	0.647		
0.48	0.687		
0.50	0.726		
0.54	0.786		
0.57	0.825		
0.69	0.859		
0.7	0.9		
0.8	0.925		
1.11	0.95		
1.76	0.975		

The probabilities of exceeding the jth threshold $P_{e,j}$ is calculated (i.e. $P_{e,6}$ = 0.125; $P_{e,5}$ = 0.157; $P_{e,4}$ = 0.194; $P_{e,3}$= 0.234; $P_{e,2}$ = 0.830; $P_{e,1}$ = 0.864). To assign plotting positions, Weibull plotting positions for uncensored observations are (Hirsch and Stedinger, 1987):

$$p(i) = (1 - P_{e,j+1}) + (P_{e,j} - P_{e,j+1})r/(A_j + 1) \quad (2)$$

where r is the rank of the ith observation among the A_j observations above the j^{th} detection limit.

In order to "fill in" data prior to estimating moment statistics, plotting positions for censored observations must be determined. In general, Weibull plotting positions for censored observations are given by (Hirsch and Stedinger, 1987):

$$pc(i) = (1 - P_{e,j})r/(C_j + 1) \quad (3)$$

where r is the rank of the ith observation among the C_j censored values known only to be less than the jth detection limit:

$$C_j = B_j - \sum_{k=0}^{j-1}(A_k + B_k) \quad \text{and } A_o = B_o = 0 \quad (4)$$

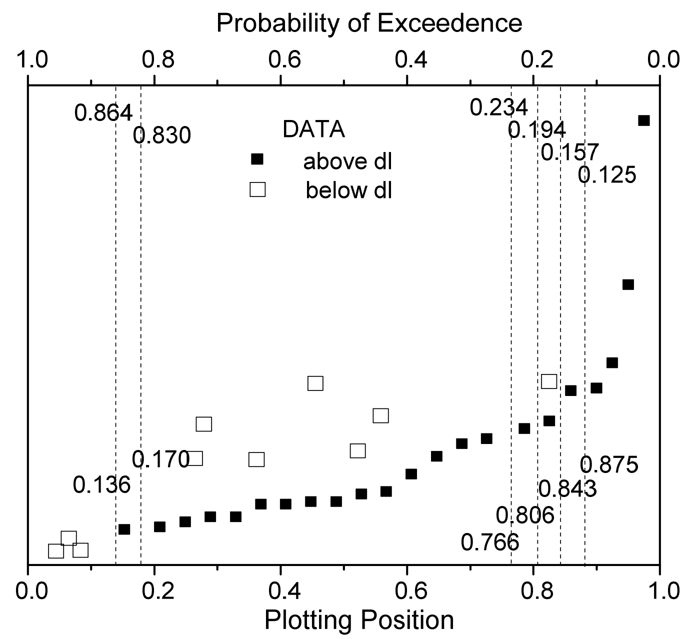

Figure 11. Plotting positions illustrated for the Pb data in 2006.

The plotting positions for both uncensored and censored Pb Data are calculated and summarized in Table 7. The plotting positions are illustrated in Figure 11. The probabilities of exceeding 6 different detection limits are shown as broken linein the figure. All the censored and uncensored observations are assigned plotting positions in the figure based on the results of calculation. Through the probability plotting method, the probability of exceedance for censored observations that under various detection limits can be determined.

5. Conclusions

This study developed a robust statistical analysis approach for pollutant loadings in urban rivers for supporting water management. The developed approaches address many existing problems in the current water quality research. A case study with real sampling data was carried out using the proposed methodology to analyze Pb level in urban rivers, and to assess its compliance with local surface water quality guideline. As per the developed approach, a series of analysis works were conducted including: a) examine the influences caused by the variations of both site conditions and timing of sampling by two-way analysis of variance (ANOVA); b) determine trends of temporal and spatial distributions of contaminant concentrations; c) include the impact of different sampling methods and teams; d) quantify uncertainties associated with the compliance assessment as per urban water quality guidelines by incorporating confidence interval concepts; e) explore the self-purification capacity of rivers by balanced two-way ANOVA; and f) analyze data obtained under different detection limitations by probability plotting method to enhance water quality analysis.

The results indicated that the changes of Pb concentration in both rivers were not statistically significant among different sites over years; the upward or downward monotonic trend of Pb concentration in each site was also not significant; no significant step trend was found by using Mann-Whitney test; interval analysis verified that the Pb concentration in 2009 and 2010 met the local surface water quality guideline; the self-purification capacities of the two rivers were much limited to reduce the concentrations of Pb in the water. Moreover, probability plotting method was adopted to investigate multiply censored water quality datasets rather than simple substitution procedures commonly used in practice. The developed approach can overcome some deficiencies of current water quality data analysis and be helpful to related management practices, particularly for protecting urban river systems. The case study demonstrated the feasibility and robustness of the approach and also indicated the potential of its application to other cases when significant changes and complexity exist in the sampling conditions and methods. However, further research is being conducted to more effectively address other uncertainties during sampling and measuring procedures.

Acknowledgments. The research was supported by MITACS, IREC, NSERC, NFSC (50709010) and the Major State Basic Research Development Program of MOST (2006CB403307).

References

Ahmed, A.L.M., Sulaiman, W.N., Osman, M.M., Saeed, E.M., and Mohammed Y.A. (2000). Groundwater quality in Khartoum state, Sudan, *J. Environ. Hydrol.*, 8, 12.

Awuah, E., Nyarko, K.B., Owusu, P.A., and Osei-Bonsu, K. (2009). Small town water quality, *Desalination*, 248, 453-459, doi:10.10 16/ j.desal.2008.05.087.

BRAGA (2001). Integrated Urban Water Resources Management: A Challenge into the 21st Century, *Water Resour. Dev.*, 17(4), 581-599, doi:10.1080/07900620120094127.

Buelna, G., and Riffat, R. (2007) Preliminary Environmental Monitoring of Water Quality in the Rio Grande in the Laredo-Nuevo Laredo Region, *J. Environ. Sci. Health*, 24(10), 1379-1390, doi:10. 1080/10934520701480383.

Canter and Maness (1995). Ground water contaminants and their sources, *Int. J. Environ. Stud.,* 47, 1-17, doi:10.1080/00207239508 710938.

Chen, B. (2008) Health-impact risk assessment for river pollution through a modified contaminant transport model. *Water Air Soil Poll.*, 200(1-4): 323-339.

Davison, A.C., and Hinkley, D. (2006). *Bootstrap Methods and their Application (8th printing)*. Cambridge: Cambridge Series in Statistical and Probabilistic Mathematics.

D'Vera C. (2005). *Investigating Washington, D.C.'s Water Quality. Nieman Reports*, 59(1), 22-23.

EPA (2010). Pb in Drinking Water. Retrieved April 1st 2010 from http://www.epa.gov/safewater/lead/.

Environmental Canada (2008). Wastewater Pollution. Retrieved April 1st 2010 from http://www.ec.gc.ca/water/en/manage/poll/e_problm. htm

Helsel, D.R., and Hirsch, R.M. (2002). Statistical Methods in Water resources, *Techniques of Water Resources Investiga- tions*, Book 4, chapter A3.

Hirsch, R.M., and Stedinger, J.R. (1987). Plotting positions for historical floods and their precision, *Water Resour. Res.*, 23(4), 715-727, doi:10.1029/WR023i004p00715.

Jin, G., Eilts, K., Kelley, T.R., and Webb, J.W. (2009). Preliminary water quality assessment of Spunky Bottoms restored wetland, *J. Environ. Sci. Health*, 44, 235-243, doi:10.1080/1093452080259777.

Li, P., Chen, B., and Husain, T. (2010). IRFAM: an integrated rule-based neural fuzzy classification system for watershed modeling. *J Hydrol Eng. ASCE*, DOI:10.1061/(ASCE)HE.1943-5584.0000 285.

Montgomeryand, J.A., and Eames, M. (2008). Prairie Wolf Slough Wetlands Demonstration Project: A Case Study Illustrating the Need for Incorporating Soil and Water Quality Assessment in Wetland Restoration Planning, Design and Monitoring, *Restoration Ecology*, 16(4), 618-628, doi:10.11 11/j.1526-100X.2008. 00492.x

Mann, H.B., and Whitney, D.R. (1947). On a test of whether one of two random variables is stochastically larger than the other, *Ann. Math. Stat.*, 18, 50-60, doi:10.1214/aoms/1177730491.

McLeod, A.I., Hipel, K.W., and Bodo, B.A. (1990). Trend analysis methodology for water quality time series, *Environmetrics*, 2, 169-200, doi:10.1002/env.3770020205.

Mkandawire, T., and Banda, E. (2009). Assessment of drinking water quality of Mtopwa village in Bangwe Township, Blantyre, Desalination, 248:557-561, doi:10.1016/j.desal.2008. 05.101.

Ipeaiyeda, A.R., and Onianwa, P.C. (2009). Impact of brewery effluent on water quality of the Olosun river in Ibadan, Nigeria, Chemistry and Ecology, 25(3), 189-204, doi:10.1080/0275754 09 02970314

Pedusaar, T., Sammalkorpi, I., Hautala, A., Salujõe, J., Järvalt, A., and Pihlak, M. (2010). Shifts in water quality in a drinking water reservoir during and after the removal of cyprinids, *Hydrobiologia*, 649(1), 95-106, doi:10.1007/s10750-010-0231 –x.

Qin, X.S., Huang, G.H., Chen, B., and Zhang, B.Y. (2009). An interval-parameter waste-load-allocation model for river water quality management under uncertainty, *Environ. Manage*, 43(6): 999-1012.

Smithson, M. (2003). Confidence intervals. *Quantitative Applications in the Social Sciences Series*, No. 140. Belmont, CA: SAGE Publications. ISBN 9780761924999.

Town of Markham (2009). Annual Regulatory Water Quality Report. Retrieved April 1st 2010 from http://www.markham.ca/NR/ rdonlyres/8E0A6DDB-EC69-4CB2-8441-62EA8E41B438/0/waterqualityreport_MOE2009.pdf

Town of Newmarket (2009). Annual Water Quality Report. Retrieved April 1st 2010 from http://www.newmarket.ca/en/townhall/ resource-library/2009AnnualWaterReport.pdf

Warner, N.R., Levy, J., Harpp, K., and Farruggia, F. (2007). Drinking water quality in Nepal's Kathmandu Valley: a survey and assessment of selected controlling site characteristics, *Hyd. J.*, 16: 321-334, doi:10.1007/s10040-007-0238-1.

Wilcoxon, F. (1945). Individual comparisons by ranking methods, *Biometrics Bulletin*, 1, 80-83, doi:10.2307/3001968.