EXHIBIT B

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Calculation of BLM Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado

Note:

This report describes the approach employed by the BLM to derive a Fixed Monitoring Benchmark (FMB). In recent editions of the BLM (v 2.2.4 and later) the method to estimate copper concentrations when an input file includes metal concentrations below detection limits (BDL) is based on the maximum likelihood (MLE) analysis. The regression on order statistics (ROS) method described in this report is no longer used, but the remaining methods used to derive the acute and chronic FMBs are the same as described herein. If estimation by MLE is needed, it is preferable that no more than 80% of the available input data are below detection limits. Flagged values as below detection limits can only be used in the column designated for copper concentrations in the worksheet.

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Introduction

The Biotic Ligand Model was recently used as the basis for an update to the U.S. EPA water quality criteria for copper (U.S. EPA 2007). The model has been widely tested and shown to be predictive of copper toxicity to a number of freshwater fish and invertebrates in a wide variety of environmental conditions. As the BLM has been applied as a tool for water quality criteria (WQC) development, it is frequently noted that the BLM calculated WQC varies from sample to sample and a means for interpreting this time variability would be useful.

The issue of time variable WQC is not unique to the BLM. The hardness equation has been commonly used in the development of WQC including the previous WQC document for copper (U.S. EPA 1985a). Despite the long-standing use of the hardness equation, the issue of time variable WQC has not been rigorously explored, in part because in the typical implementation of the hardness equation the time-variable water quality would simply be averaged to generate a constant WQC. The recently developed ammonia WQC is another example of a criteria methodology where time-variability needs to be considered.

In using the BLM, the awareness of important factors other than hardness has been heightened and some of what we now know to be important parameters for determining metal toxicity (such as pH and DOC) are consistently time-variable. The purpose of this document will be to look at the effect of time-variable water chemistry on BLM results, and to use a probability-based method for developing a fixed-site criterion from time-variable results.

Description of Approach

The approach presented here for the calculation of fixed monitoring benchmarks (FMB) for copper (Cu) is a probability-based method that incorporates time variability in BLM-predicted instantaneous water quality criteria (IWQC) and in-stream Cu concentrations. The phrase "fixed monitoring benchmark" is used, rather than "fixed site criteria" because it more accurately reflects the purpose of this value, being that it is a benchmark that can be used to evaluate compliance with WQC. One of the major differences between this approach and WQC, as described below, is that FMB will depend, in-part, on existing Cu concentrations, whereas WQC are dependent upon the characteristics of the receiving water, independent of Cu concentrations. The FMB is a value that will produce the same toxic unit distribution exceedence frequency as the time variable IWQC would produce for a given monitoring dataset.

This approach relies upon the distribution of toxic units (TU), calculated as:

$$TU_i = \frac{Cu_i}{IWQC_i}, \qquad \text{Eqn. 1}$$

where TU_i is a single TU value calculated for a single sample collected at time i, Cu_i is the Cu concentration in this sample, and $IWQC_i$ is the BLM-based IWQC calculated for this sample. The calculation of TU_i requires that all of the BLM input parameters needed to calculate IWQC and the measured Cu concentration are available for this sample. The distribution of TU values for all of the samples collected at a site is then used to estimate the probability that an in-stream Cu concentration equals or exceeds its associated IWQC, in other words the probability that TU $\geq$ 1.

Although understanding whether the current Cu concentrations are above or below IWQC values is useful, the intent of this analysis is to determine the distribution of Cu concentrations that is in compliance with associated IWQC. The magnitude of the Cu concentrations comprising the compliant Cu distribution (i.e., $Cu_{i,comp}$), may be higher or lower than the magnitude of the Cu concentrations comprising the existing Cu distribution (Cu_i), however, the relative magnitude can be estimated from the existing copper concentrations by comparing the current exceedence frequency (i.e., the probability that the current $TU_i \geq 1$) with a target exceedence frequency (EF). The target EF in this analysis is once in three years, as recommended by the water quality criteria guidance document (Stephan et al., 1985), however alternative EFs can be used.

The distribution of Cu concentrations in compliance with the IWQC can be estimated from the existing distribution and the target EF. If the probability that $TU_i \geq 1$ is less than the target EF, then the magnitude of the values comprising the distribution of Cu concentrations in compliance with the IWQC is greater than the magnitude of the Cu values comprising the current Cu distribution ($Cu_{i,comp} > Cu_i$) and conversely if the probability that $TU_i \leq 1$ is greater than the target EF, then $Cu_{i,comp} < Cu_j$.. In estimating $Cu_{i,comp}$ it is assumed that the standard deviation of the log-transformed $Cu_{i,comp}$ values is equal to the standard deviation of the log-transformed Cu_i values.

To illustrate this approach, consider a hypothetical situation in which an effluent with a median Cu concentration of 20 μg/L and a coefficient of variation (CV) of 0.5 is introduced to a stream where values for BLM input parameters are known. In this example, the effluent is introduced at a flow rate that is 10% of the receiving water body (i.e. a stream) flow, and the in-stream dissolved copper concentration can be calculated based on mass-balance between the effluent and upstream sources (although for simplicity lets assume that the effluent is the only source of Cu). In this hypothetical situation, the receiving water, downstream of the effluent, is sampled 1 time per month for a 30 month period, and in-stream Cu concentrations and IWQC values are compared for this 30 month dataset. Figure 1a shows a time series plot of IWQC and dissolved copper during this 30 month period, showing variation of values over time. Figure 1b shows the same data as a probability plot, where both the IWQC and dissolved copper values are plotted in order from the lowest observed values to the highest observed values. Both IWQC and dissolved copper are log-normally distributed. In the time series plot, IWQC and dissolved copper concentrations are paired by date, but that temporal

pairing is not obvious in the probability plot, since both distributions are ordered from low to high, regardless of the date on which they were sampled.

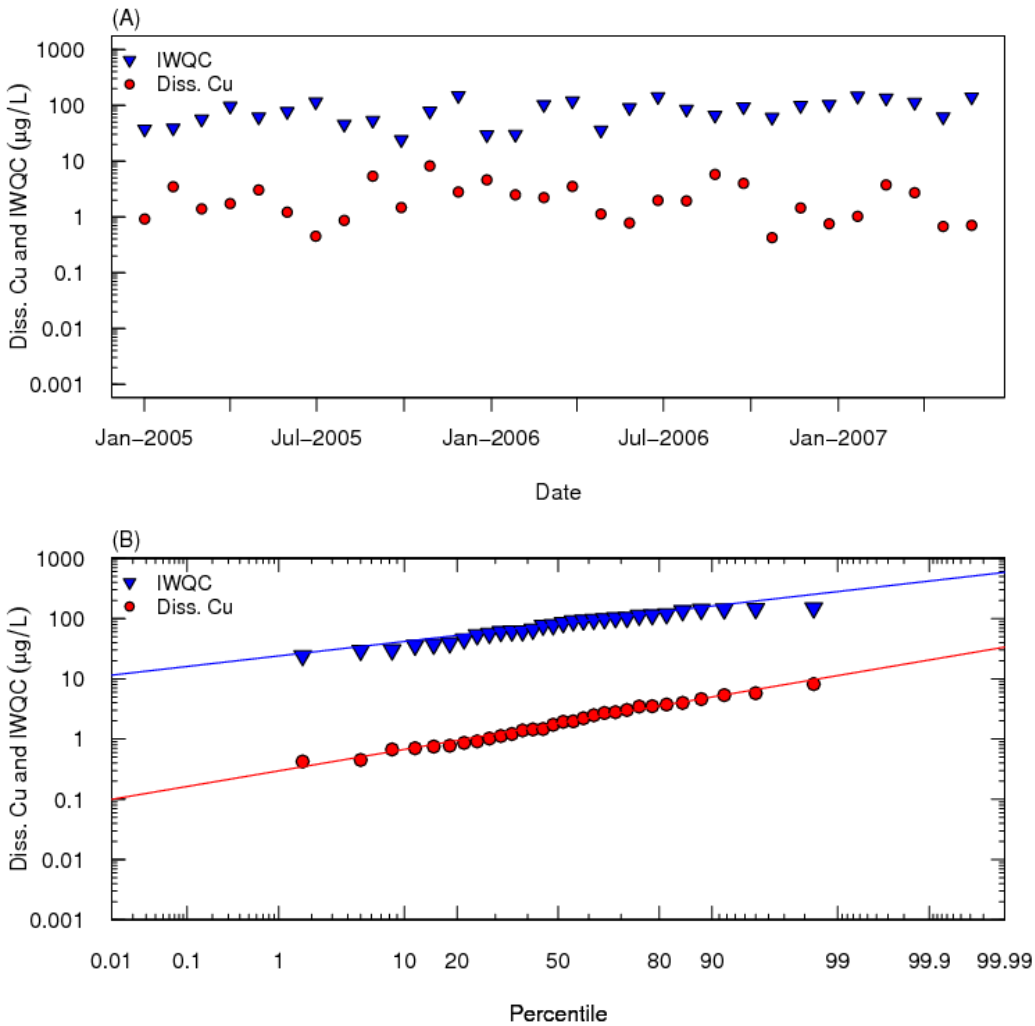

Figure 1. Hypothetical example of effluent with median Cu concentration of 20µg/L coefficient of variation of 0.5 introduced to stream with no Cu. The flow rate of the effluent is 10% of the flow rate of the receiving water. The top panel shows BLM-predicted instantaneous water quality criteria (IWQC) and in-stream Cu concentrations (Diss. Cu) plotted as a time series, in which 1 sample per month was collected over a 30 month period. The bottom panel shows the same data as a cumulative probability plot. The colored lines in the bottom panel represent linear descriptions of the cumulative probability distributions for the same colored data points.

For this hypothetical example, the TU_i values, calculated as described by Eqn. 1, are shown in Figure 2. In Figure 2a, TU_i values are plotted over time for each sampling event, and in Figure 2b the cumulative probability distribution of these values is illustrated. To determine if the Cu concentrations are expected to exceed the IWQC more frequently than the target EF, we can examine the probability that TU_i at the target EF

(TU_{EF}) ≥ 1 and compare that to EF. An EF of once in 3 years corresponds to 1 day out of 1095 days, or a relative frequency of 0.00913. Therefore, the TU distribution should have values such that $TU_i > 1$ no more frequently than 1/1095, which is equivalent to saying that $TU_i < 1$ 99.91% of the time (i.e. 100*(1.000-0.000913)). The vertical line on the probability plot at 99.91% corresponds to the target EF and for Cu concentrations to be in compliance, the TU_i should cross this EF at a value of 1 or less.

Extrapolation of the TU distribution to the specified EF of once every 3 years demonstrates that the estimated TU at this point (i.e. TU_{EF}) is less than 1. This suggests that the dissolved Cu concentrations in this hypothetical stream are lower than they need to be to be protective of aquatic life. Equation 2 shows how the TU_{EF} can be calculated from the summary statistics of the TU values:

$$TU_{EF} = 10^{[Z_{EF} * s_{TU} + \log_{10}(TU_{Median})]}, \qquad \text{Eqn. 2}$$

where Z_{EF} is the number of standard deviations that the EF is from the median using a standard normal distribution, s_{TU} is the standard deviation of the log-transformed TU values, and TU_{Median} is the median TU. With an EF of 1/1095, the Z_{EF} is 3.117. From TU_{EF}, it is possible to estimate the distribution of Cu concentrations that will exactly meet the TU_{EF}, and therefore, by definition this distribution would be composed of Cu concentrations that are in compliance with the time variable IWQC (called $Cu_{i,\,comp}$ in the equations that follow). This distribution can be estimated from the existing Cu distribution and TU_{EF} if it is assumed that the variance in toxic units is the same for both the existing Cu concentrations and the distribution in compliance with the IWQC. To estimate $Cu_{i,comp}$, an adjustment factor (AF) is defined that can be applied to the Cu distribution that will result in a $TU_{EF} = 1$, i.e.:

$$AF = \frac{1}{TU_{EF}}. \qquad \text{Eqn. 3}$$

In this example, $TU_{EF} = 0.4802$, so the AF is 2.083 (Figure 2b). The AF can then be applied to the dissolved Cu values, resulting in compliant Cu concentrations ($Cu_{i,comp}$):

$$Cu_{i,comp} = Cu_i * AF, \qquad \text{Eqn. 4}$$

so that the compliant TU distribution, with $TU_{EF} = 1$, is composed of values represented by:

$$TU_{i,comp} = \frac{Cu_{i,comp}}{IWQC_i}. \qquad \text{Eqn. 5}$$

The adjusted Cu and TU distributions are represented by the dashed lines in Figure 3b. These lines demonstrate how these distributions would look if the in-stream Cu concentrations were adjusted by the AF. From the revised in-stream Cu distribution, it is

possible to calculate the acute fixed monitoring benchmark (FMB_a), which is the Cu concentration at the specified EF:

$$FMB_a = 10^{[Z_{EF} * s_{Cu} + \log_{10}(Cu_{Median,comp})]}, \qquad \text{Eqn. 6}$$

where $Cu_{Median,comp}$ is the median of the compliant Cu distribution, and s_{Cu} is the log standard deviation of the original Cu distribution. For this example, $Cu_{Median,comp}$ = 3.810 µg/L (which is equivalent to the original Cu_{Median} multiplied by the AF), s_{Cu} = 0.3397, and Z_{EF} = 3.117, resulting in an FMB_a = 43.63 µg/L, as calculated by Eqn. 6. This value, along with the associated AF is shown on Figure 3b as the point at which the revised in-stream Cu distribution meets the specified EF.

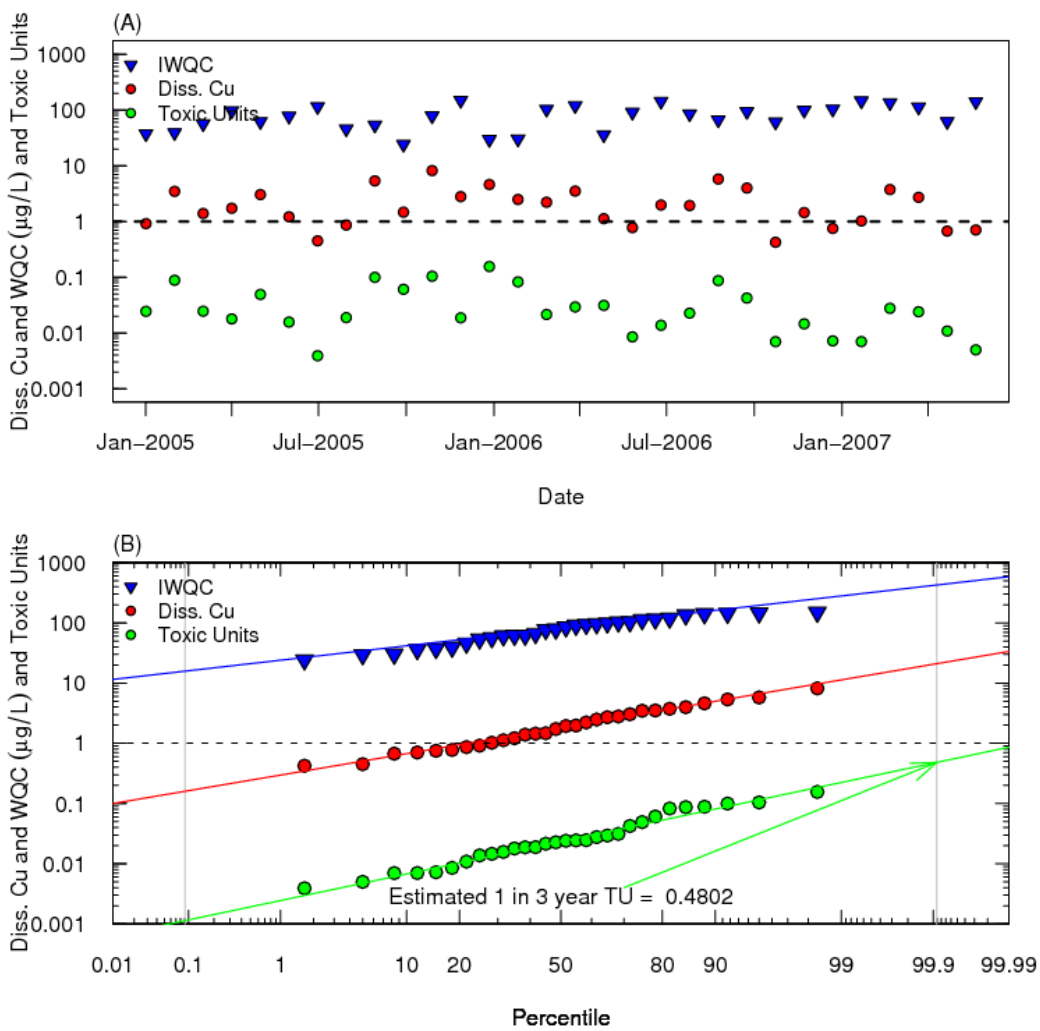

Figure 2. Hypothetical example with conditions the same as those described in the caption for Figure 1. The top panel shows BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Diss. Cu), and toxic units plotted as a time series, in which 1 sample per month was collected over a 30 month period. The bottom panel shows the same data as a cumulative probability plot. The colored lines in the bottom panel represent linear descriptions of the cumulative

probability distributions for the same colored data points. In both panels, the horizontal dashed line indicates a toxic unit of 1.

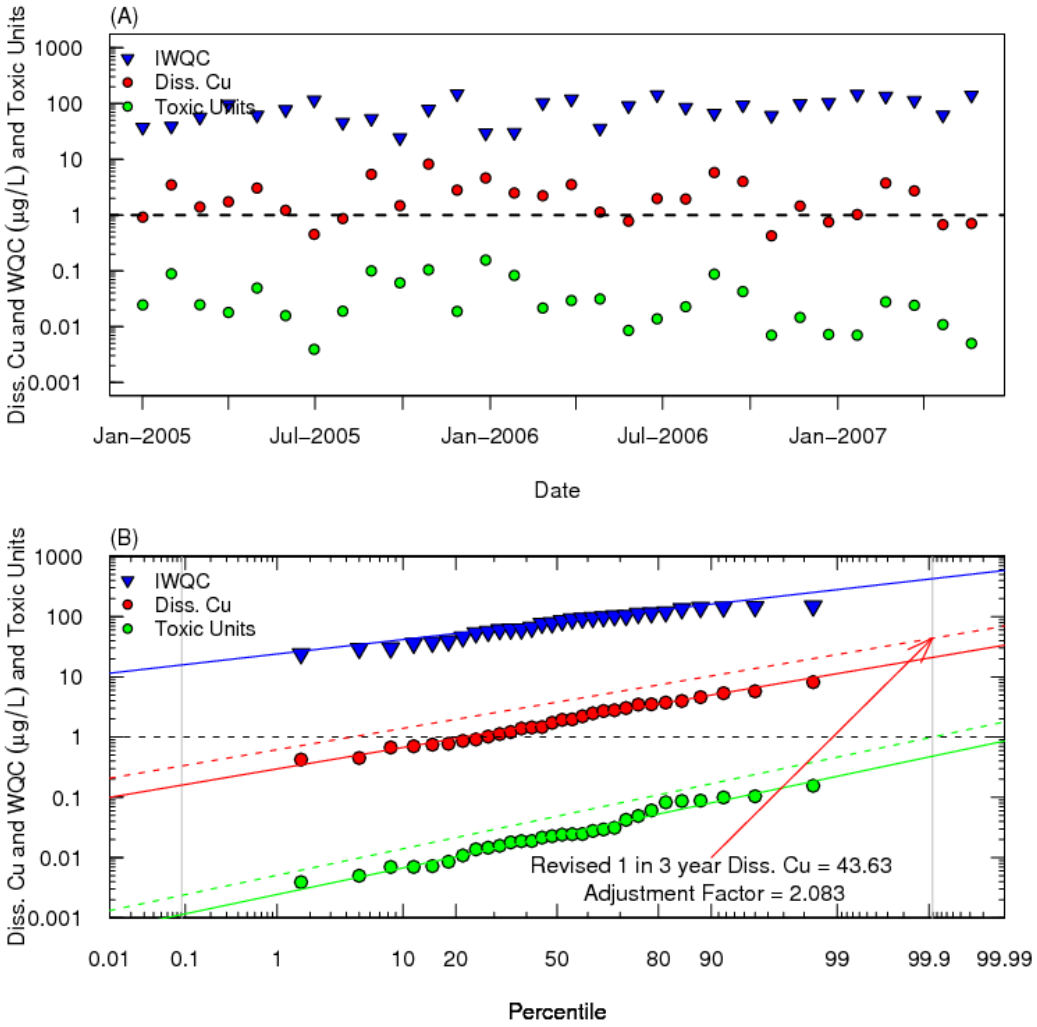

Figure 3. Hypothetical example with conditions the same as those described in the caption for Figure 1. The top panel shows BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Diss. Cu), and toxic units plotted as a time series, in which 1 sample per month was collected over a 30 month period. The bottom panel shows the same data as a cumulative probability plot. The solid colored lines in the bottom panel represent linear descriptions of the cumulative probability distributions for the same colored data points, and the dashed lines represent revised distributions that meet the specified exceedence frequency of once every three years. In both panels, the horizontal dashed line indicates a toxic unit of 1.

To further demonstrate this principle with the hypothetical example, the amount of copper in the effluent is increased by the AF, so that the median concentration of copper in the effluent is now 41.66 µg/L. The in-stream Cu concentrations and the TU values in Figure 4a are now elevated with respect to their original values (Figures 1-3). Figure 4b

demonstrates that the TU distribution of this example meets the specified EF, with a $TU_{EF} = 1.0$.

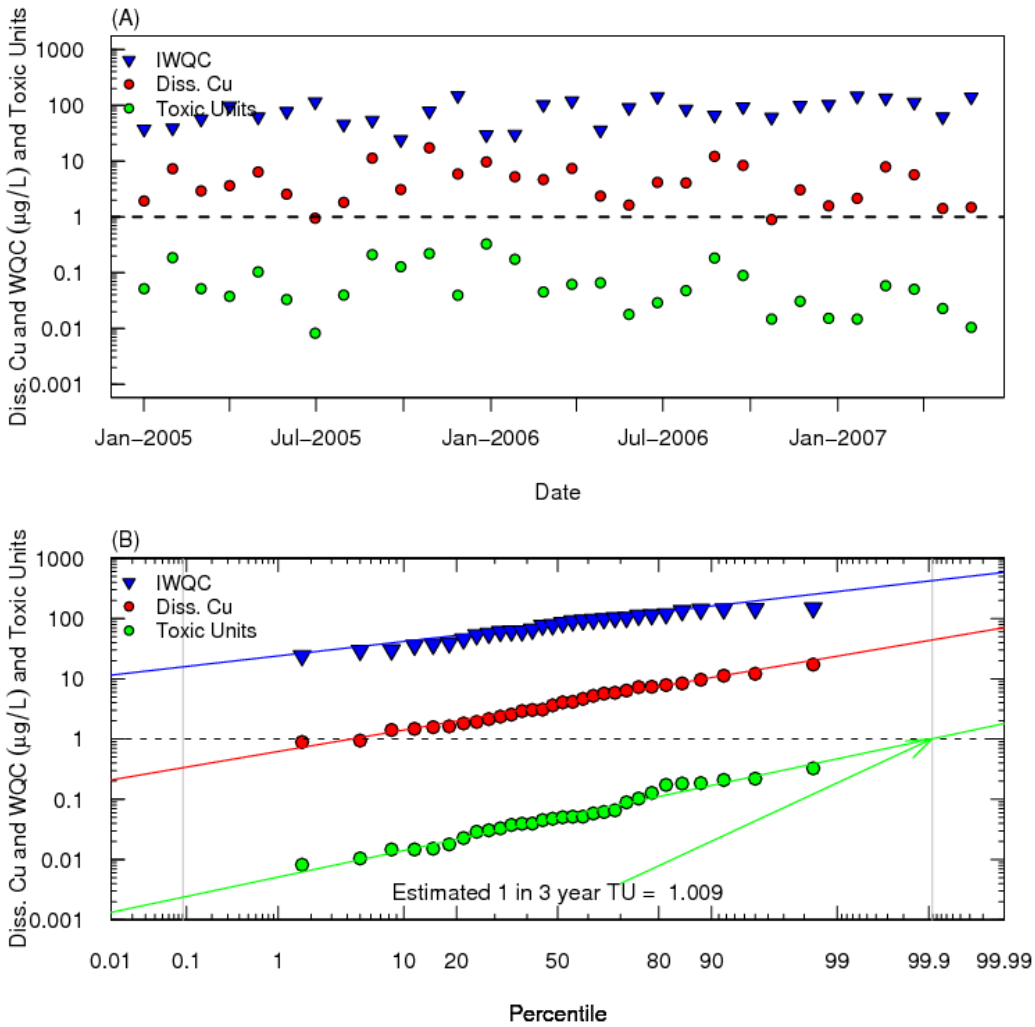

Figure 4. Hypothetical example with median Cu concentration in effluent is increased by the factor suggested by the probability analysis. The median Cu concentration in the effluent is now 41.66 g/L (i.e. 2.083*20 g/L), with a coefficient of variation of 0.5. The top panel shows BLM-predicted instantaneous water quality criteria (IWQC), in-stream Cu concentrations (Diss. Cu), and toxic units plotted as a time series, in which 1 sample per month was collected over a 30 month period. The bottom panel shows the same data as a cumulative probability plot. The colored lines in the bottom panel represent linear descriptions of the cumulative probability distributions for the same colored data points. In both panels, the horizontal dashed line indicates a toxic unit of 1

As described above, the summary statistics that are required for this approach are the log median and the log standard deviation of the in-stream Cu and TU data, with the assumption that the distributions are log normal. Here we use the log median because it is an unbiased and consistent estimate of the log mean (Zar 1999), when the values are log normally distributed. Further, the median is less affected by detection limit issues that are common to environmental samples (Helsel 1990). So, assuming that the

quantities of interest (i.e. IWQC, Diss. Cu, and TU) are log normally distributed and that the log median is a good estimate of the log mean, the respective distributions will be symmetric around the log median.

This approach is straightforward and results in a simple calculation to determine FMB_a. When non-detects are present in the in-stream Cu data, the approach becomes somewhat more complicated, because a regression approach is required to fit the distributions in order to estimate the summary statistics. The regression method that was used here is an implementation of a regression on order statistics (ROS)[1] designed specifically for analytical chemistry data that contain non-detect values (Helsel 1990; Lee and Helsel 2005).

In addition to calculation of FMB_a, the approach can be modified to determine chronic fixed monitoring benchmarks (FMB_c) by using BLM IWQC that are adjusted by the acute to chronic ratio (ACR), and by adjusting the variability in in-stream Cu grab samples to be consistent with the variability that would be appropriate for 4-day averages.

This approach and the examples presented above demonstrate that the BLM can be used in conjunction with in-stream Cu concentrations to establish both FMB_a and FMB_c based upon historical monitoring data. An important assumption of this approach is that the slope of the cumulative probability distributions does not change when an adjustment factor is applied. That is, the log standard deviation of the adjusted distribution is the same as the log standard deviation of the original distribution.

Description of the Data Used to Evaluate this Approach

Several data sets, provided by the state of Colorado, were used to develop case-studies to test the application of the probability-based approach (Appendix A). This data set encompassed 5 different river/creek systems, including the South Platte River, Boulder Creek, Cache la Poudre River, Fountain Creek, and Monument Creek. Within these systems, water chemistry and/or in-stream Cu concentrations were reported for 70 different locations (and 7 effluent samples), most of which were within the South Platte River system. The combined datasets provided 4914 observations where some water chemistry and/or in-stream copper concentrations were available. Unfortunately only 277 of the 4914 observations included measurement for all BLM input parameters as well as copper, which are required in order to be usable for this analysis. However, a sensitivity analysis on BLM input values (described below) indicated that it was acceptable to estimate the values for some BLM inputs when values were not reported. This increased the amount of data usable for this analysis to 415 of the 4914 observations, with most of those (i.e., 339) coming from the South Platte River system.

[1] In recent editions of the BLM (v 2.2.4 and later) the method to estimate copper concentrations when an input file includes metal concentrations below detection limits (BDL) is based on the maximum likelihood (MLE) analysis. The regression on order statistics (ROS) method described in this report is no longer used.

Methods Used to Analyze the Available Data

The individual data sources from reports and tables (Sarah Johnson, personal communication; Lareina Wall, personal communication) were organized into a single large database containing sampling dates, in-stream Cu concentrations, and water chemistry information needed for BLM analyses including pH, dissolved organic carbon (DOC) concentration, water hardness, and ion concentrations. This database was used as the source for all BLM input files that were created for this analysis. In many cases, some of the required BLM inputs were missing from individual samples, or missing entirely from all of the samples taken at a given monitoring location. As an example, available data for the South Platte River sites Cent_Min_Ave and DEH-N14 are shown in Figures 5 and 6. At the Cent_Min_Ave monitoring site (Figure 5), the available data include values for dissolved Cu, DOC, pH, sulfate (SO_4), alkalinity, and hardness, but are missing Ca and Mg measurements. In cases like this, where Ca and Mg are missing but hardness is measured, the individual ion concentrations were estimated from hardness assuming a Ca:Mg ratio of 2.1417 for the South Platte River. At the DEH-N14 monitoring location the available data included values for all BLM inputs except alkalinity. Alkalinity is typically considered an important input to the model, and measurements are required for BLM calculations. However the relatively small percentage of data in the overall database that contained measurements for all BLM inputs made it desirable to determine whether some of the missing parameters could be estimated. Parameter estimation allowed the inclusion of relatively rich monitoring data such as DEH-N14 where one or more BLM input parameters were missing.

The data for BLM input parameters shown in Figures 5 and 6 show that values for these parameters show considerable variation over time. In some cases there seemed to be recurring patterns, possibly indicating seasonal variation (such as for Alkalinity at Cent_Min_Ave shown in Figure 5), suggesting that seasonal analyses of BLM results may provide interesting insights and could be explored in subsequent work at these locations. Long-term trends were also suggested in some of the individual measurements, such as the increasing alkalinity values at Cent_Min_Ave (Figure 5) that might indicate changing conditions. In other cases there were changes in measured values over time that indicated changes in analytical protocols had possibly affected the monitoring data results. For example, compare the relatively erratic total organic carbon (TOC) measurements in Cent_Min_Ave from dates in 2000 and 2001, with subsequent dissolved organic carbon (DOC) measurements in 2002 (Figure 5). Detection limits for some analyses also seemed to change over time, as indicated by the presence of data plotted with hollow symbols on these data plots (for example dissolved copper values in Figure 5). All of these issues highlight the need for data quality reviews as part of any ongoing BLM monitoring program. Another useful means for viewing the overall variation in input parameter values and detecting potential inconsistencies and quality issues is through the use of probability plots as shown in Figures 7 and 8. In performing these example calculations, data quality issues were discussed with the project team as part of our regular conference calls (and in particular with personal communications with Lareina Wall), but rigorous data QA was beyond the scope of our intended project.

Similar figures were developed for each of the 77 monitoring data sets considered for this analysis can be viewed in sections 3 and 4 of Appendices D through H. From these figures, it is possible to assess availability and variability of the data required for this analysis. Because many sites lacked some data that were necessary for the analysis, a sensitivity analysis (described below) was conducted to determine if estimated values could be used when input values were not reported.

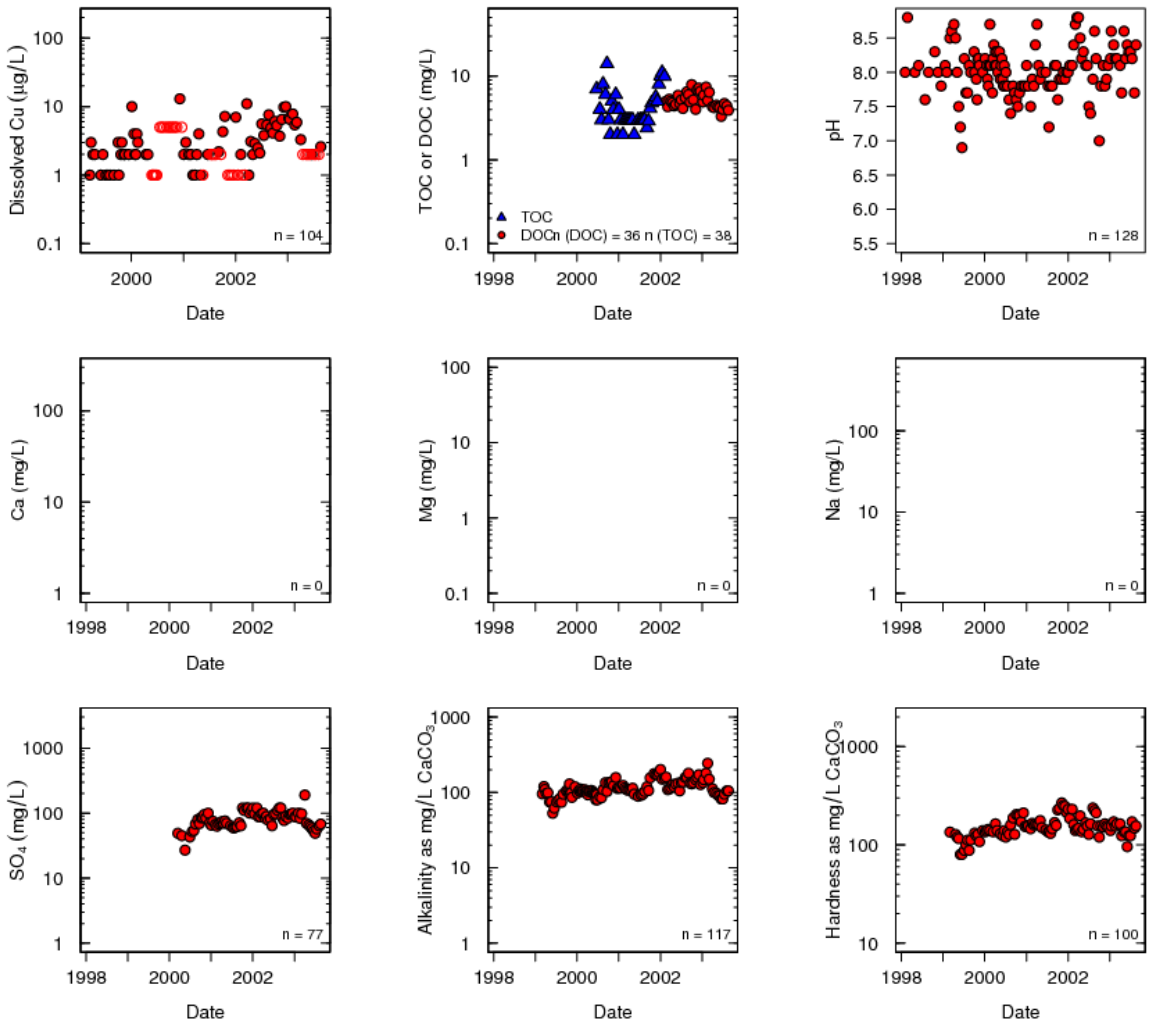

Figure 5. Time series plots of available BLM input data for the Cent_Min_Ave site from South Platte River.

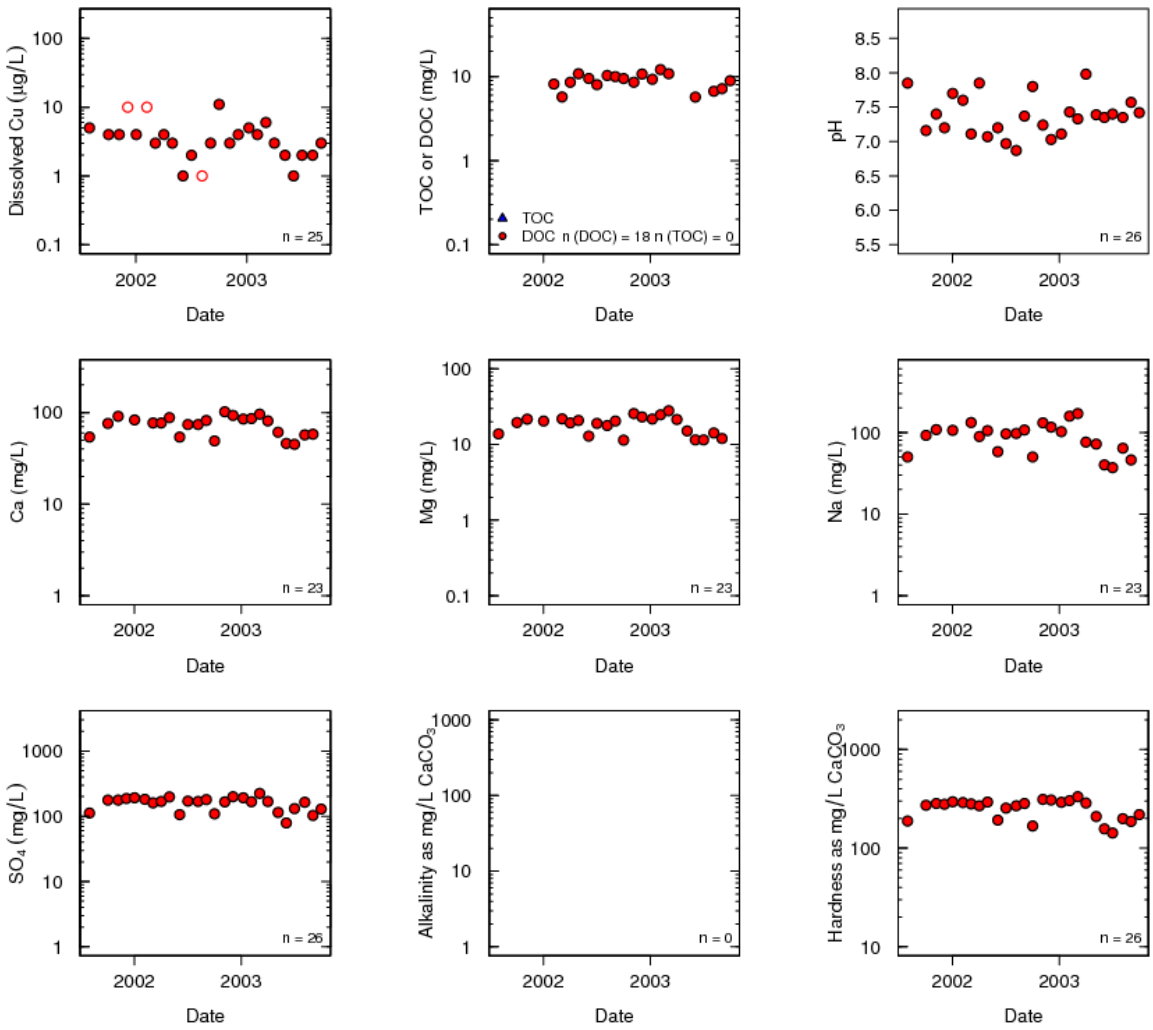

Figure 6. Time series plots of available BLM input data for the DEH-N14 site from the South Platte River

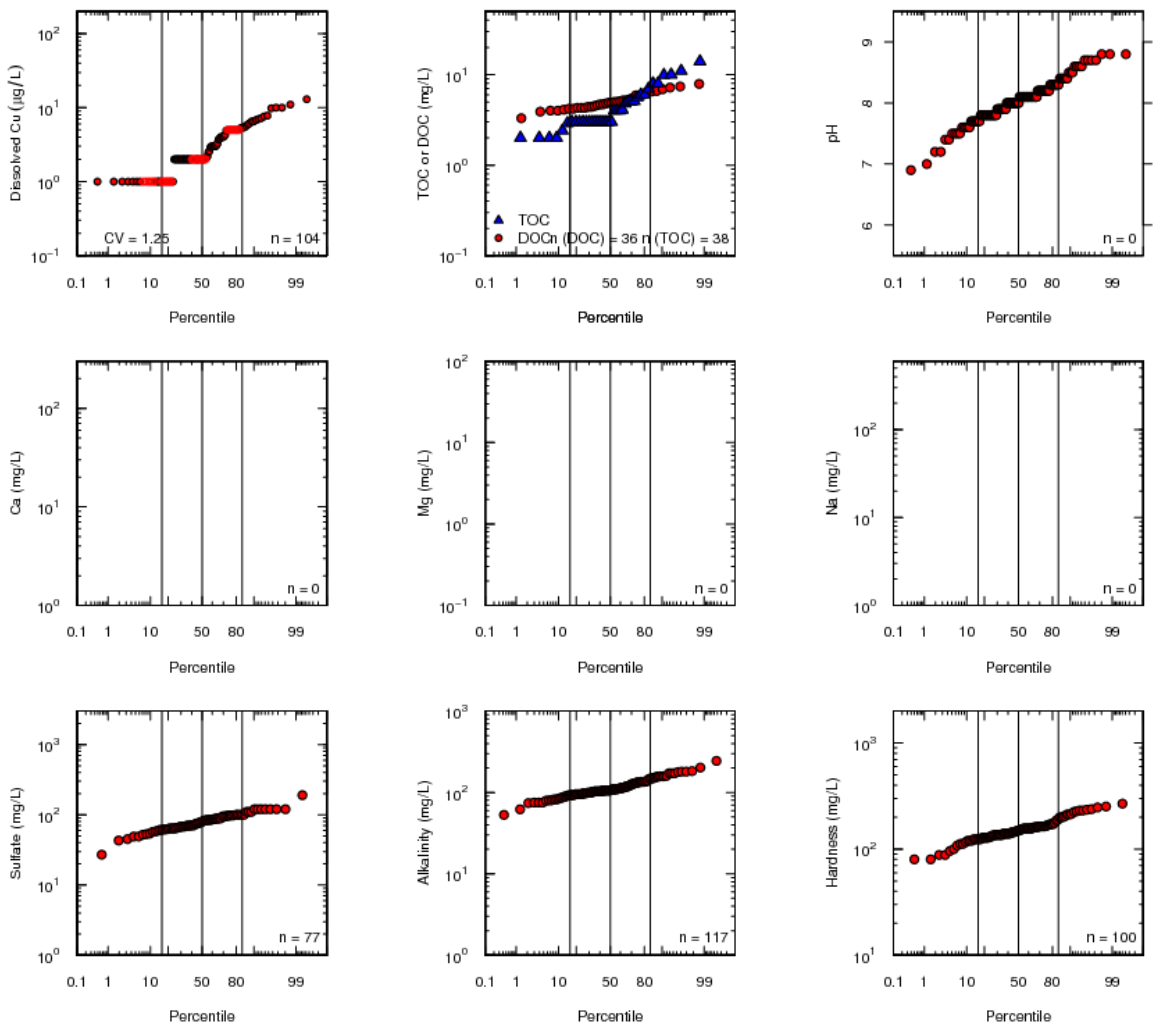

Figure 7. Probability plot of available BLM input data for the Cent_Min_Ave site from South Platte River.

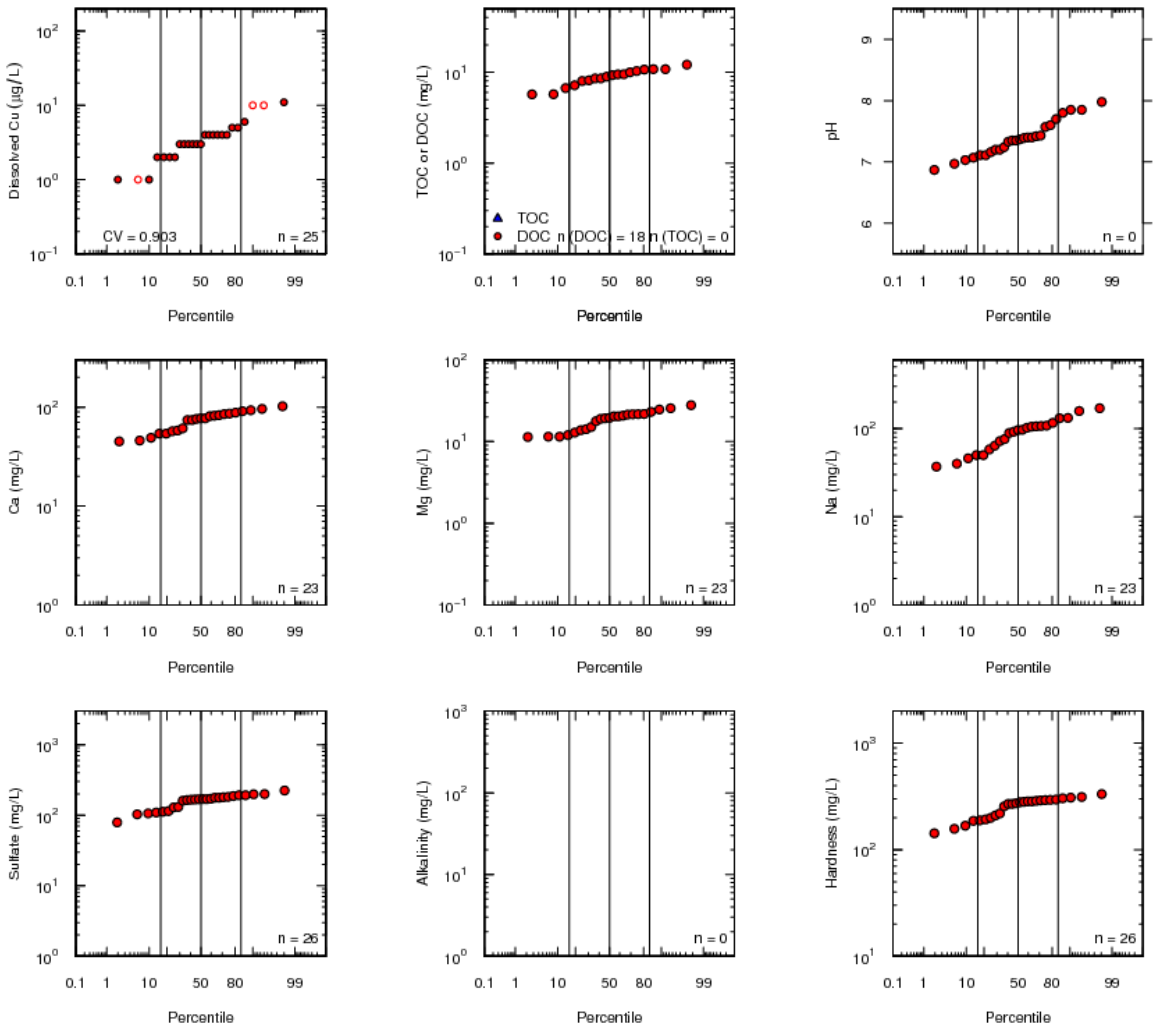

Figure 8. Probability plot of available BLM input data for the DEH-N14 site from the South Platte River.

The sensitivity analysis was used to determine the relative importance of different input variables on determining the IWQC values. Since it was only necessary to predict IWQC, Cu concentrations were not required, thereby allowing a larger number of usable observations than was used for the determination of FMB. The base data set for the sensitivity analysis included 732 separate observations. Several steps were required for the sensitivity analysis. First, the BLM was used to calculate IWQC for the base data set. This provided IWQC for the case in which all BLM inputs available and fixed at their reported values. The second step involved using the BLM to calculate IWQC for the cases where BLM inputs were fixed at the minimum value for the entire Colorado Rivers data set. This was done separately for each input parameter. For example, when the minimum pH was used, the pH inputs for all 732 observations in the BLM input file were fixed at the minimum pH (Table 1) and the other BLM inputs remained at their original reported values. Separate BLM input files were prepared in this fashion for each of the BLM input parameters listed in Table 1, for a total of 7320 lines of BLM input. The third

step was to calculate IWQC for the cases where BLM inputs were fixed at the maximum value for the entire Colorado Rivers data set. This procedure was analogous to the case where minimum values were used, except that the maximum values for each parameter (Table 1) were used, totaling another 7320 lines of BLM input. The fourth step was to calculate IWQC at the mean or geometric mean value (geometric mean was used for all inputs except pH and temperature) for each BLM input from the entire Colorado Rivers data set, totaling another 7320 lines of BLM input. This provided an indication of whether or not it would be acceptable to use the mean values for various BLM inputs when values were not reported.

Figure 9 and Figure 10 show the results of the sensitivity analysis for the Cent_Min_Ave and DEH-N14 sites, respectively. The results of all other sensitivity analyses can be viewed in section 5 of Appendices D through H. This analysis demonstrated that for temperature, Ca, Mg, Na, K, SO4, Cl, and alkalinity, geometric mean values (from the entire Colorado Rivers data set) could be used without affecting the IWQC predictions, but that pH and DOC inputs must be based upon measured/reported values. The results of the sensitivity analysis were consistent across all sites in this database, suggesting that the most important BLM input parameters for the Colorado Rivers data set are pH and DOC. Because of the sensitivity of these results on both pH and DOC, it was determined that estimates for these parameters would have too large an impact on the results. Sites where either pH or DOC was not measured, therefore, were excluded from any further BLM analyses. Therefore, the only site-specific data required for the subsequent probability analyses were: in-stream Cu concentration, pH, and DOC concentration. The other input values, when missing, were set to the geometric mean values from the Colorado Rivers data set (Table 1).

Table 1. Minimum, mean, and maximum values of BLM input parameters from the Colorado Rivers data set.

BLM Input Parameter	Minimum	Mean*	Maximum
Temperature (^{o}C)	-0.2	13.32	30.5
pH	5.7	7.7	9.7
DOC (mg/L)	1.0	7.1	42.0
Ca (mg/L)	5.2	65.8	471
Mg (mg/L)	0.12	18.6	133
Na (mg/L)	4.2	82	609
K (mg/L)	0.58	6.43	25.7
SO_4 (mg/L)	7.99	161	2560
Cl (mg/L)	0.79	60.85	845
Alkalinity (mg $CaCO_3$/L)	0.116	150	980

*Geometric mean used for all but Temperature and pH

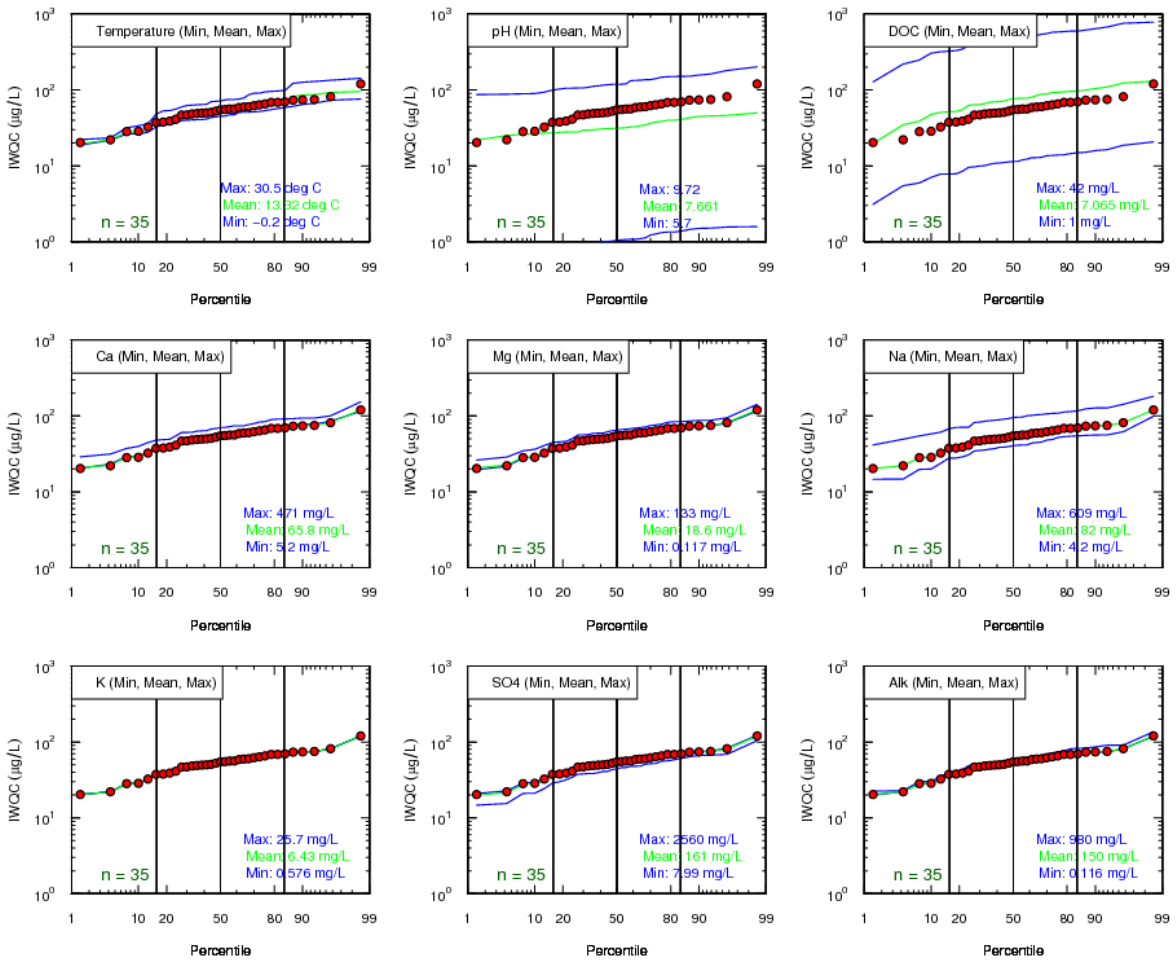

Figure 9. Sensitivity analysis for the Cent_Min_Ave site from South Plate River. The red symbols in each panel show the IWQC predictions for the base data set, where each BLM input value was fixed at its reported value. The blue lines in each panel show the sensitivity of IWQC predictions to the minimum and maximum values of each BLM input parameter. Each panel contains a label in the top left portion of the figure that describes the BLM parameter investigated. The IWQC is also shown (green line) for each case in which the BLM input parameter was set to the data set geometric mean (arithmetic means were used for temperature and pH).

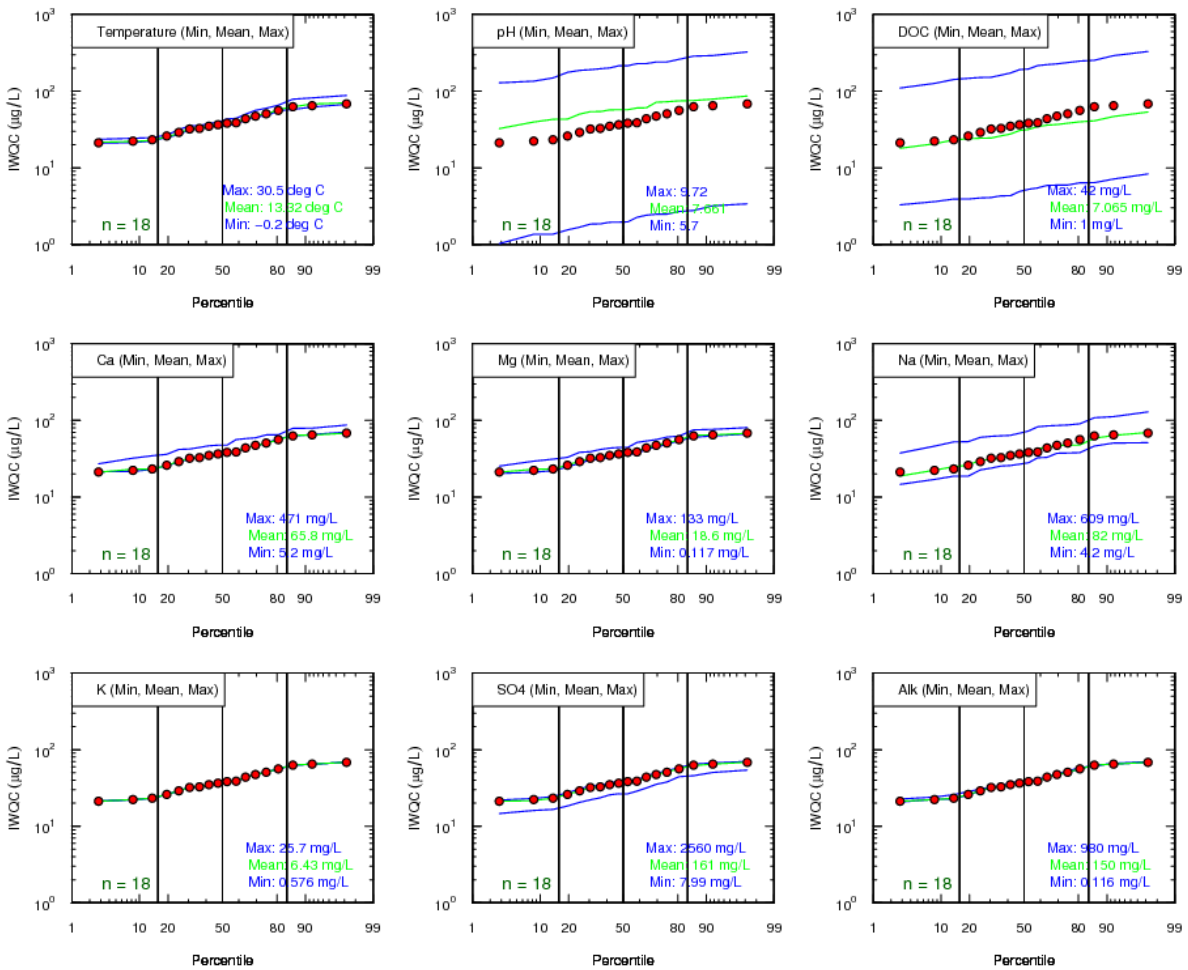

Figure 10. Sensitivity analysis for the DEH-N14 site from the South Platte River. The red symbols in each panel show the IWQC predictions for the base data set, where each BLM input value was fixed at its reported value. The blue lines in each panel show the sensitivity of IWQC predictions to the minimum and maximum values of each BLM input parameter. Each panel contains a label in the top left portion of the figure that describes the BLM parameter investigated. The IWQC is also shown (green line) for each case in which the BLM input parameter was set to the data set geometric mean (arithmetic means were used for temperature and pH).

It is important to note that the relative lack of sensitivity to cation and anion concentrations in these datasets may not be observed at other sites. It is not uncommon, for example, to see sites where the BLM analysis shows hardness cations to be more important than there were in these data. Therefore, these results should not be used as a rationale for not measuring cations and anions at other sites, or even in subsequent monitoring at these sites.

Because the sensitivity analysis demonstrated that geometric means could be used for the values of missing BLM inputs, 415 observations (i.e. lines of BLM input) were usable for the probability-based analysis. However, as mentioned above, some of the in-stream Cu concentrations for some sites were reported as a detection limit or less than a specified detection limit. Those data were useful for the probability-based analysis, because they

provided some information related to the relative abundance of low vs. high in-stream Cu. Further, when detection limit values are present in a data set, the underlying distribution can be estimated from the uncensored values (i.e. values above a detection limit) in the data set by using a method for regression on order statistics (Helsel 1990; Lee and Helsel 2005). When detection limits were present in this dataset, the regression on order statistics method was implemented with the "ros" function from the "NADA" package for the R statistical program and computing environment (R Development Core Team 2008). This procedure was viewed as absolutely necessary for this probability-based approach, since the calculation of FMB depends upon the summary statistics of the in-stream Cu and TU data, and because detection limit values were present in most of the data sets examined. The regression on order statistics approach provides an appropriate method for determining the summary statistics of an underlying distribution when detection limits are present.

Results of the Analysis

The probability approach described above was applied to the Colorado Rivers BLM data set, using both the BLM-based IWQC and the hardness-based water quality criteria (HWQC) to calculate FMB_a. The HWQC was calculated for each site with the mean hardness from the associated site-specific BLM data set. To calculate the FMB_a on the basis of HWQC, the denominator in Eqn. 1 is simply replaced with $HWQC_i$, and subsequent calculations are the same as the described for the BLM-based approach (Eqns. 2-6).

Figure 11 shows the time series and distributions of IWQC, in-stream Cu, and TU for the Cent_Min_Ave site from the South Platte River. The detection limit values are shown as unfilled symbols and the line representing the distributions (Figure 11b) were fit using the regression on order statistics method described above. The analysis shows that the TU_{EF} is less than 1, suggesting that the in-stream Cu distribution can be increased by application of the AF to meet the specified exceedence frequency. The revised in-stream Cu concentrations and TU values are shown in the time series plot (Figure 12a), and the revised distributions are shown in Figure 12b. Based upon the available data and the method described above, the FMB_a for Cent_Min_Ave is 46.5 µg/L (Figure 12b). The same analysis is shown for DEH-N14 in Figure 13 and Figure 14. With DEH-N14, the AF is 3.09, and the resulting FMB_a is 60.7 µg/L. The results from all sites with adequate BLM input data are summarized in Tables 2 and 3, and similar figures representing this analysis for each site can be viewed in the section 7 of Appendices D through H. Table 2 shows the results of this analysis when it was applied to site water, and Table 3 shows the results of this analysis when it was applied to effluent samples.

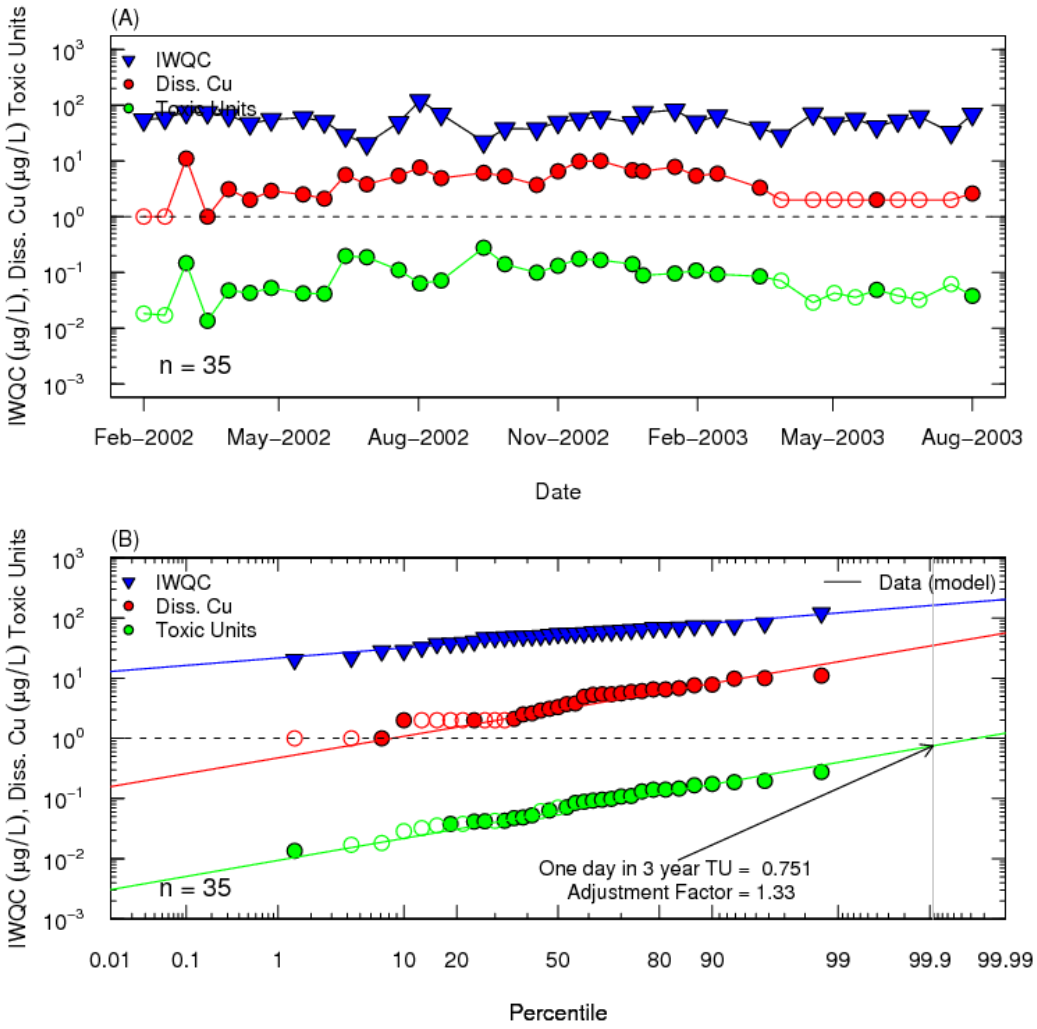

Figure 11. Time series (A) and probability plot for the in-stream Cu (Diss. Cu), IWQC and toxic units (TU) from Cent_Min_Ave from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The arrow indicates the extrapolated TU value at the EF, and the resulting adjustment factor (AF) is shown.

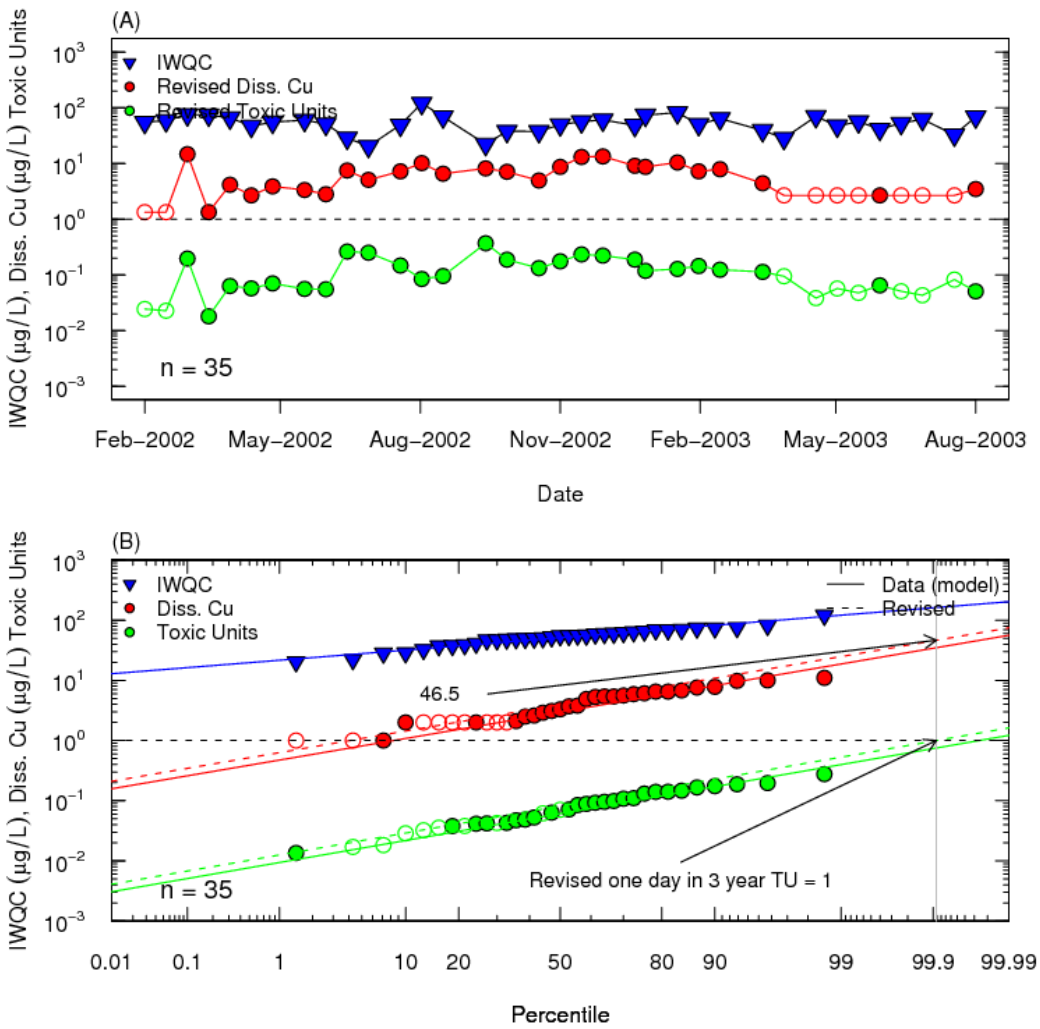

Figure 12. Time series (A) and probability plot (B) showing revised in-stream Cu (Diss. Cu), IWQC and revised TU from Cent_Min_Ave from the South Platte River. The horizontal dashed line represents a TU= 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The upper arrow indicates the FMB_a, and the lower arrow indicates the TU_{EF} = 1.

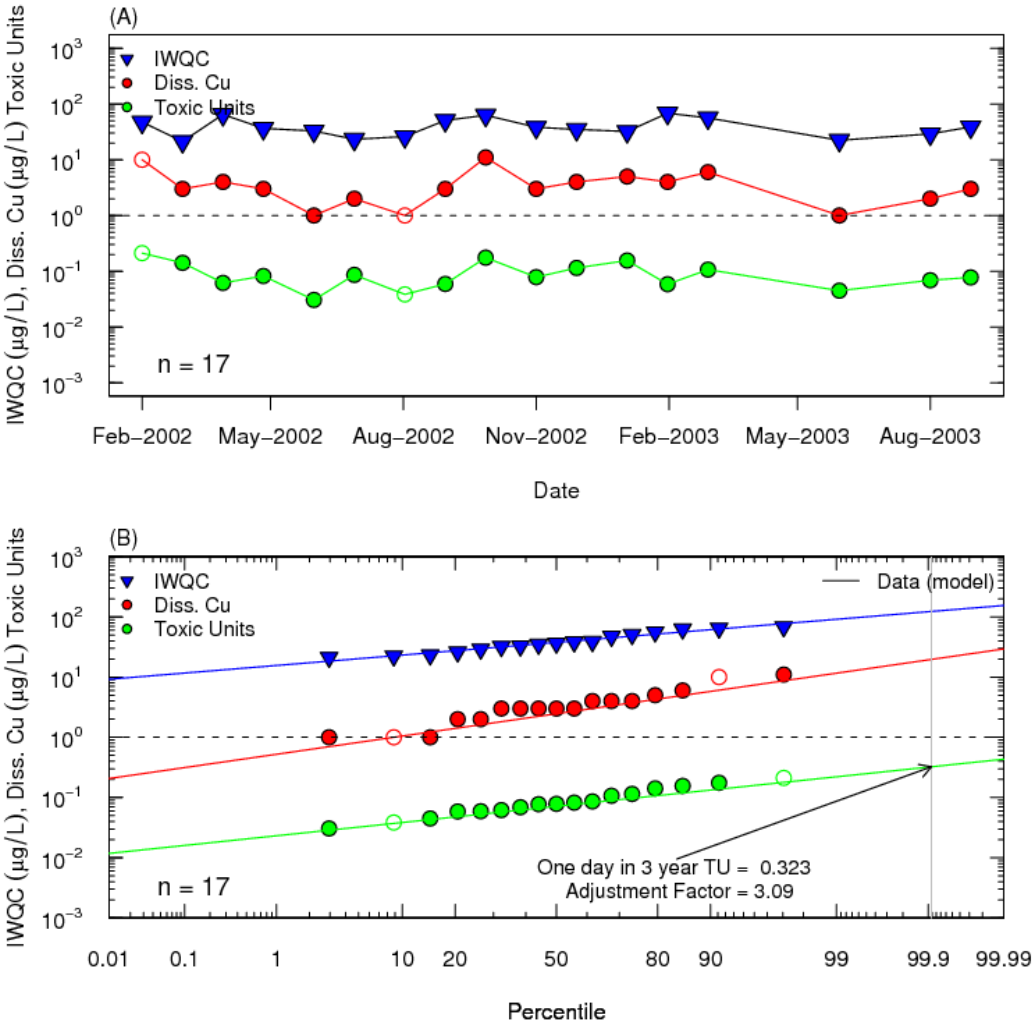

Figure 13. Time series (A) and probability plot (B) for the in-stream Cu (Diss. Cu), IWQC and TU from DEH-N14 from the South Platte River. The horizontal dashed line represents a TU=1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red line) or TU values that were calculated with detection limit in-stream Cu values (green series). The arrow indicates the extrapolated TU values at the EF, and the resulting adjustment factor (AF) is shown.

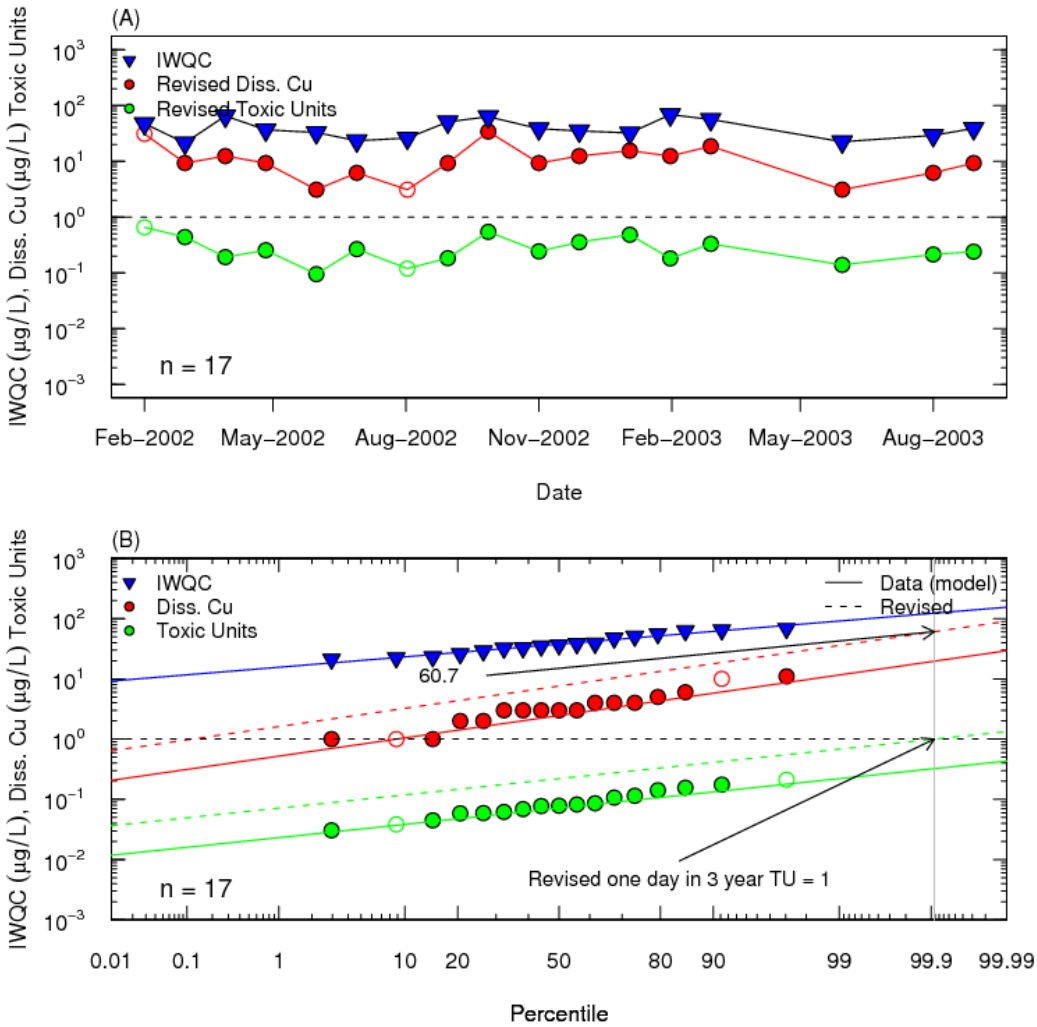

Figure 14. Time series (A) and probability plot (B) showing revised in-stream Cu (Diss. Cu), IWQC and revised TU from JEH-N14 from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The upper arrow indicates the FMBa, and the lower arrow indicates that the TUEF = 1.

The same procedure was used to calculate FMB_a when the HWQC were used, and those results are shown in Figures 15-18. It can be seen from Figures 16 and 18 that the FMB_a, when the hardness equation is used, is simply the HWQC. This is easily explained by the fact that HWQC is constant, and the condition at which $TU_{EF} = 1$, is where the revised in-stream Cu concentration equals the HWQC. Since HWQC is constant, the FMB_a will always be equal to the HWQC at the specified exceedence frequency. The results of the analysis using the HWQC are summarized in Tables 2 and 3, and similar figures representing this analysis for each site can be viewed in the section 8 of Appendices D through H.

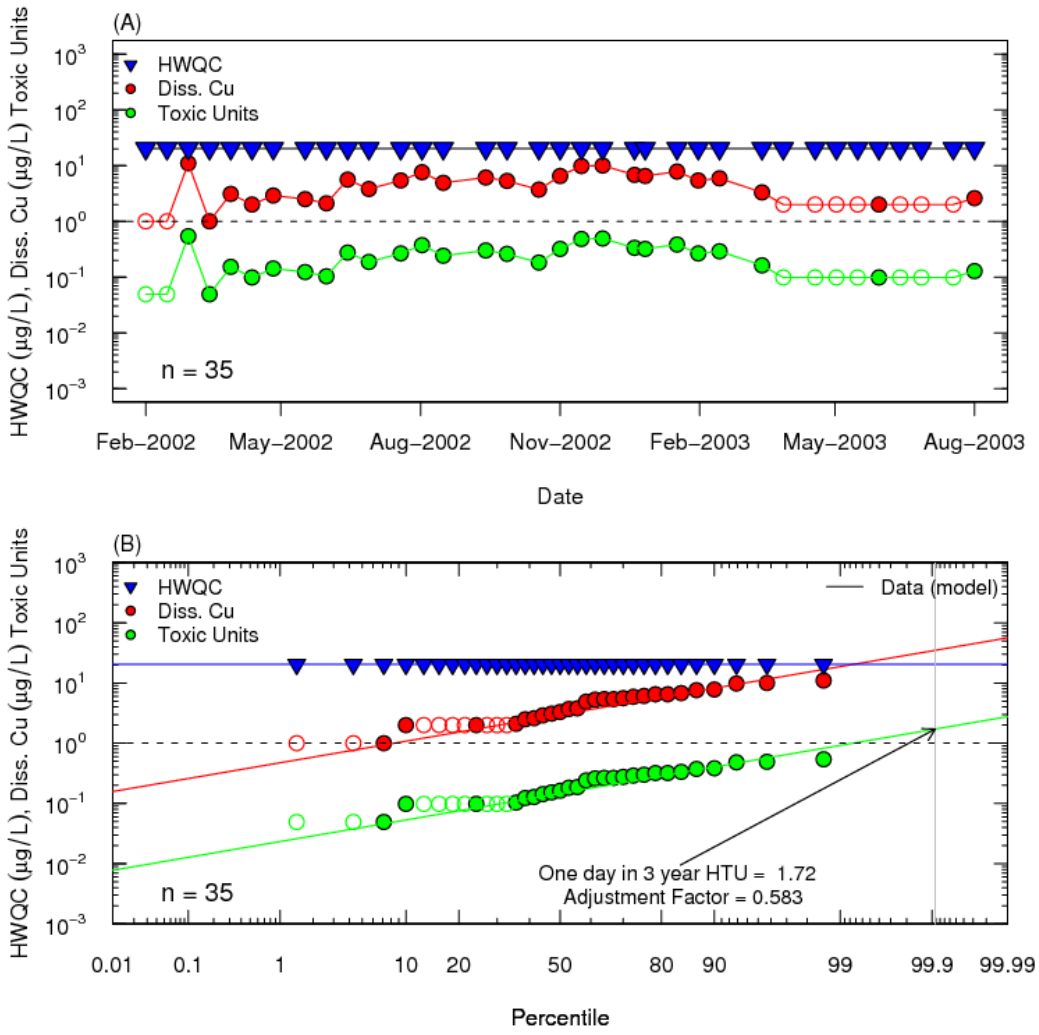

Figure 15. Time series (A) and probability plot (B) for the in-stream Cu (Diss. Cu), HWQC and TU from Cent_Min_Ave from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The arrow indicates the extrapolated TU value at the EF, and the resulting adjustment factor (AF) is shown.

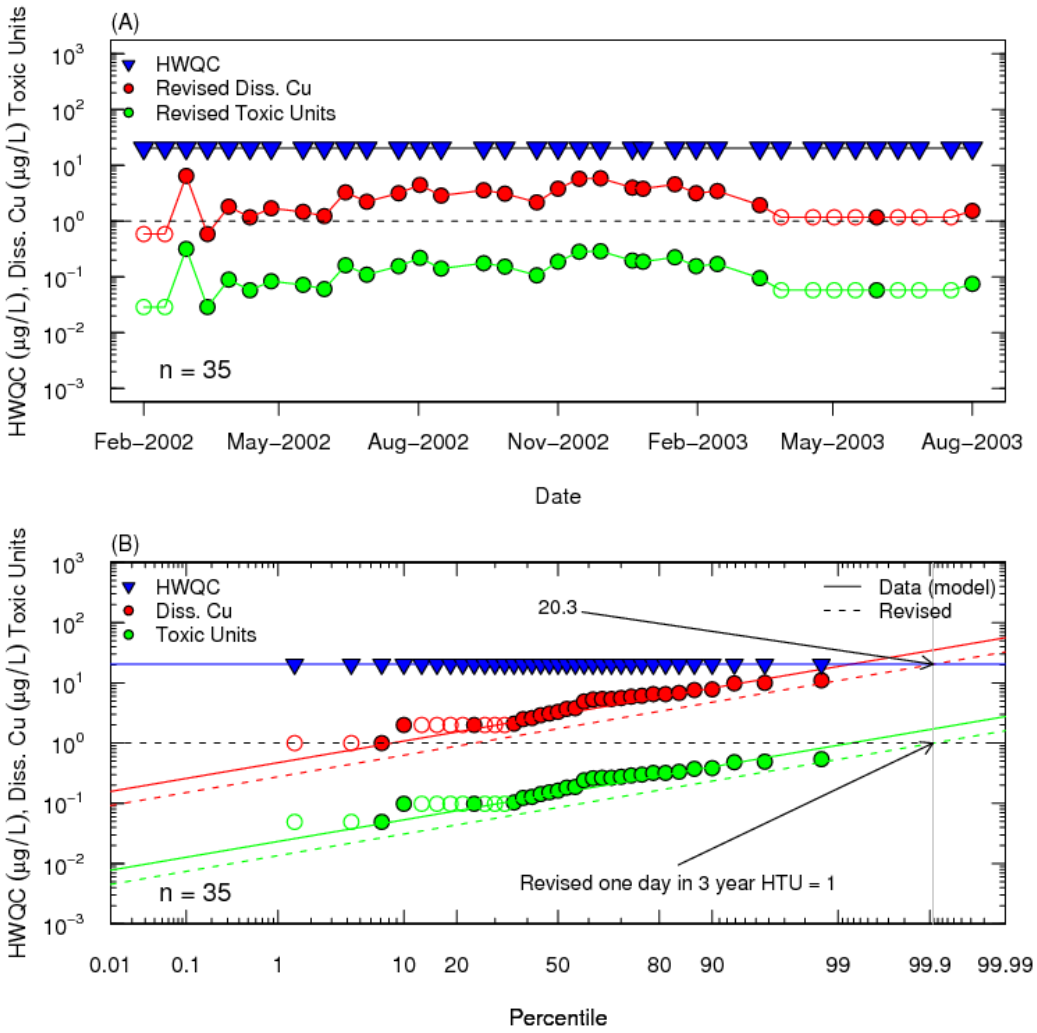

Figure 16. Time series (A) and probability plot (B) showing revised in-stream Cu (Diss. Cu), HWQC and revised TU from Cent_Min_Ave from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The upper arrow indicates the FMBa, and the lower arrow indicates that the TUEF = 1.

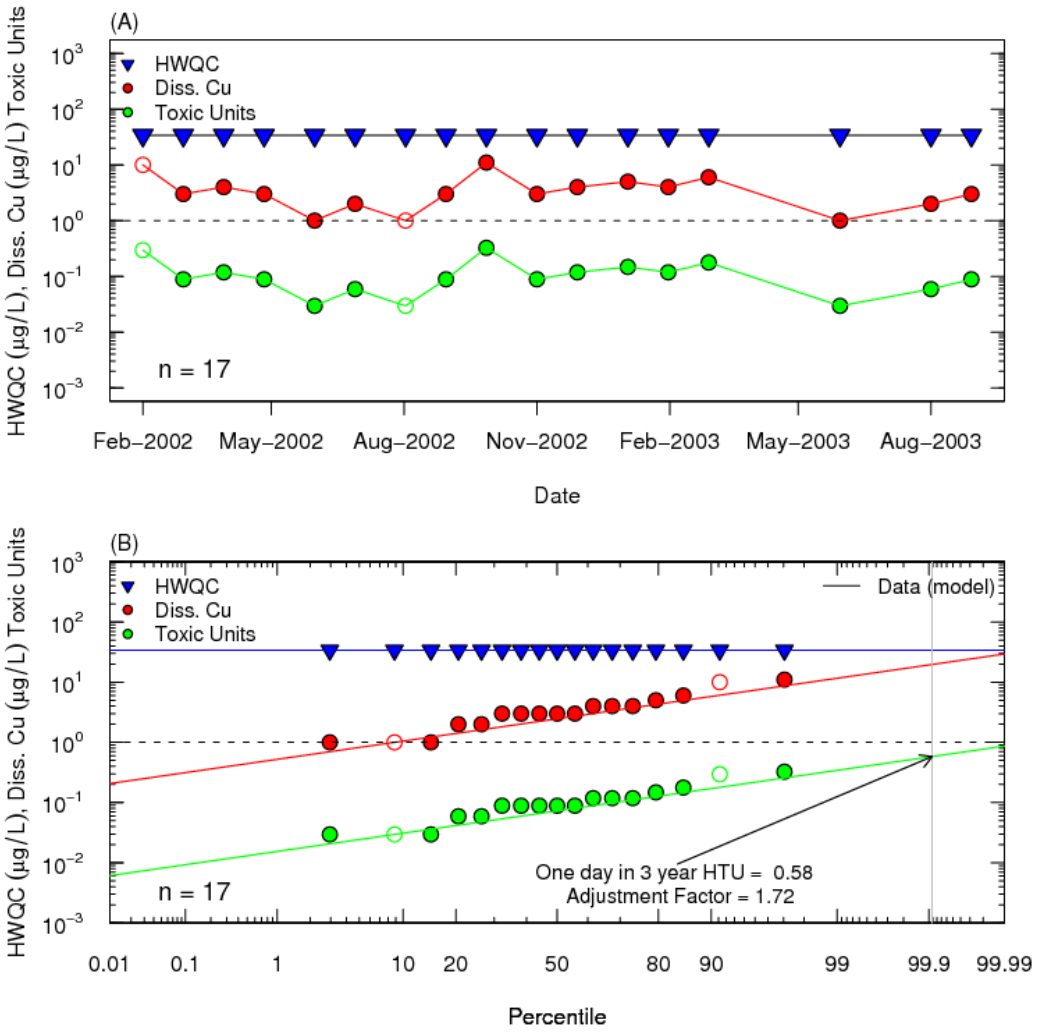

Figure 17. Time Series (A) and probability plot (B) for the in-stream Cu (Diss. Cu), HWQC and TU from DEH-N14 from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The arrow indicates the extrapolated TU value at the EF, and the resulting adjustment factor (AF) is shown.

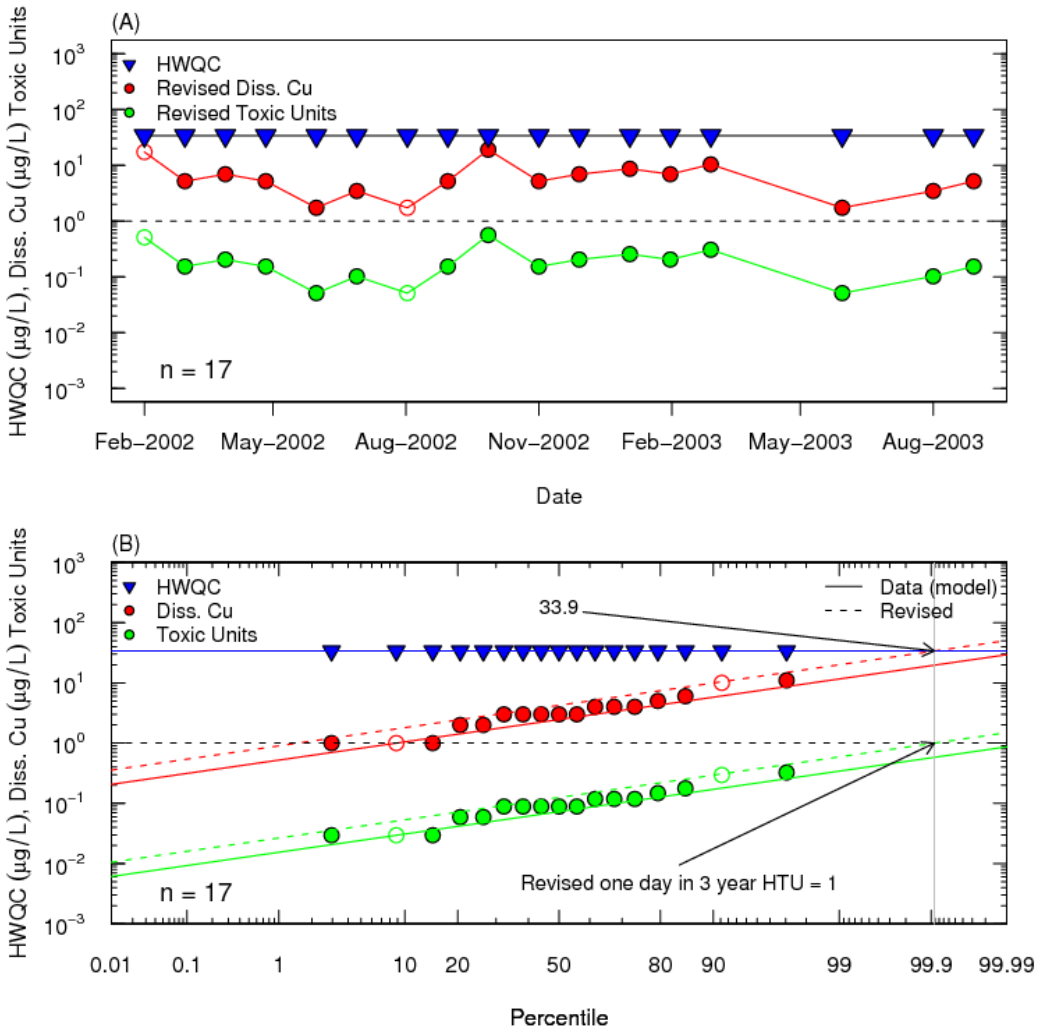

Figure 18. Time series (A) and probability plot (B) showing revised in-stream Cu (Diss. Cu), IWQC and TU from DEH-N14 from the South Platte River. The horizontal dashed line represents a TU = 1, and the grey vertical line represents the exceedence frequency (EF) of once every three years. Unfilled symbols represent values that were reported as a detection limit value (red series) or TU values that were calculated with detection limit in-stream Cu values (green series). The upper arrow indicates the FMBa, and the lower arrow indicates that the TUEF = 1.

Table 2. Results of the probability method to calculate acute FMB using both the BLM-based IWQC and hardness-based HWQC. Results are for site waters. To calculate the HWQC, the hardness equation was applied to the mean hardness for a given BLM data set, providing constant HWQC. If a water effect ratio (WER) was available for a given location, the site specific criterion obtained by adjusting the hardness equation results is provided in the column labeled HWQC*WER. The summary statistics used to calculate the FMBa with the BLM-based IWQC can be viewed in Appendix B.

					BLM IWQC Method		Hardness Equation Method	
River System	Station ID	Location	n	Cu Median (ug/L)	IWQC Median (ug/L)	Cu FMB_a (ug/L)	HWQC (ug/L)	HWQC*WER (ug/L)
Monument	Baptist	Baptist Rd.	49	2.55	29.9	65.2	13.0	
Monument	North_gate	Northgate Blvd.	21	2.62	32.0	59.2	15.6	
South_Platte	Aurora_Down	39° 45.667' N 105° 51.950' W	12	2.43	47.9	52.4	49.6	129*
South_Platte	Aurora_Up	39° 45.417' N 105° 50.817' W	12	1.34	64.5	142.0	49.6	
South_Platte	River_Down	39° 59.633' N 104° 49.552' W	24	5.42	41.8	29.1	29.2	
South_Platte	River_Up	39° 59.528' N 104° 49.709' W	26	5.86	44.7	37.4	30.0	
South_Platte	Cent_Min_Ave	39° 34.917' N 105° 01.867' W	35	2.97	51.1	46.5	20.3	54.9**
South_Platte	DEH-N14	39° 44.312' N 105° 01.083' W	17	2.46	37.7	60.7	33.9	
South_Platte	DEH-N25E	39° 45.274' N 105° 00.511' W	17	2.42	50.1	32.6	33.5	
South_Platte	DEH-N38	39° 46.155' N 104° 58.996' W	17	2.64	54.2	14.9	36.4	
South_Platte	DEH-N46	39° 47.030' N 104° 58.524' W	17	2.77	70.2	38.5	35.5	
South_Platte	S_Adams_Up	39° 52.457' N 104° 54.815' W	33	1.23	40.9	221.0	29.3	

* WER for Aurora_Down is 2.6
** WER for Cent_Min_Ave is 2.7
BLM = Biotic Ligand Model
IWQC = BLM-based Instantaneous Water Quality Criteria
FMB_a = Acute Fixed Site Criterion
HWQC = Hardness-based Water Quality Criteria
WER = Water Effect Ratio

Table 3. Results of the probability method to calculate acute FMB using both the BLM-based IWQC and hardness-based HWQC. Results are for effluents. To calculate the HWQC, the hardness equation was applied to the mean hardness for a given BLM data set, providing constant HWQC.

					BLM IWQC Method		Hardness Equation Method
River System	Station ID	Location	n	Cu Median (ug/L)	IWQC Median (ug/L)	Cu FMB_a (ug/L)	HWQC (ug/L)
Cache_la_Poudre	Drake	Drake WRF	3	10.2	38.4	8.1	25.4
Cache_la_Poudre	Mulberry	Mulberry WRF	3	7.19	57.1	9.5	25.4
South_Platte	Aurora_Eff	39° 45.683' N 105° 51.283' W	12	3.68	26.3	20.3	34.8
South_Platte	Effluent	39° 59.558' N 104° 49.619' W	26	7.05	33.5	38.3	21.8
South_Platte	MG_Effluent	39° 33.417' N 105° 02.117' W	35	13.4	50.3	45.3	24.8
South_Platte	Effluent	39° 42.350' N 104° 56.167' W	25	5.44	43.7	71.6	21.5
South_Platte	S_Adams_Eff	39° 52.443' N 104° 54.746' W	31	18.5	91.8	61.3	39.1

BLM = Biotic Ligand Model
IWQC = BLM-based Instantaneous Water Quality Criteria
FMB_a = Acute Fixed Site Criterion
HWQC = Hardness-based Water Quality Criteria

The results in Table 2 show that the BLM-based FMB_a is generally higher than the hardness-based FMB_a although for four of the sites the two methods produced nearly equivalent results (Aurora_Down, River_Down, DEH_N25E, and DEH-N46). At two of the sites, the BLM result was moderately higher (River_Up, and DEH-N14), and at five of the sites the BLM result was substantially higher than the hardness equation based water quality criteria (Baptist, North_gate, Aurora_Up, Cent_Min_Ave, and S_Adams_Up). In the remaining case at DEH-N38 the hardness-based FMB_a is substantially higher than the BLM-based FMB_a and possible reasons for this will be discussed subsequently.

The results for Aurora_Up and Aurora_Down illustrate an important limitation of the hardness-based approach, since the mean hardness is >400 mg $CaCO_3$/L in both of these cases, and therefore the HWQC and the hardness-based FMB_a for these two sites is fixed at 49.6 μg/L (the HWQC for a sample with 400 mg $CaCO_3$/L). The BLM approach suggests that the FMB_a should be higher in both cases.

For sites where monitoring data were collected both upstream and downstream of an effluent discharge, the BLM result in the downstream location was typically much lower than the upstream site (e.g., compare River_Up with River_Down, and Aurora_Up with Aurora_Down). This suggests that the effluent that is introduced to the South Platte River (e.g. Aurora_Eff; Table 3) between the upstream and downstream monitoring locations is affecting the IWQC at the downstream location. The primary constituent that appears to be responsible for this difference in FMB_a at the upstream and downstream locations is pH. The median pH from the Aurora_Up samples is nearly 7.9, and the median IWQC is approximately 60 μg/L (Figure 19). The median pH in the effluent samples (Aurora_Eff) is much lower, with a median of 7.2, and the median IWQC in the effluent is approximately 25 μg/L (Figure 20). It can also be seen that the Ca and Mg concentrations are lower in the effluent samples (Note: box and whisker plots were prepared for all sites that were included in this analysis, and they can be viewed in section 6 of Appendices D through H). Hence, it is not surprising that the median pH in the Aurora_Down samples is approximately 7.6, with a median IWQC of approximately 45 μg/L, since the downstream samples reflect the mixing of effluent with the South Platte River at this location.

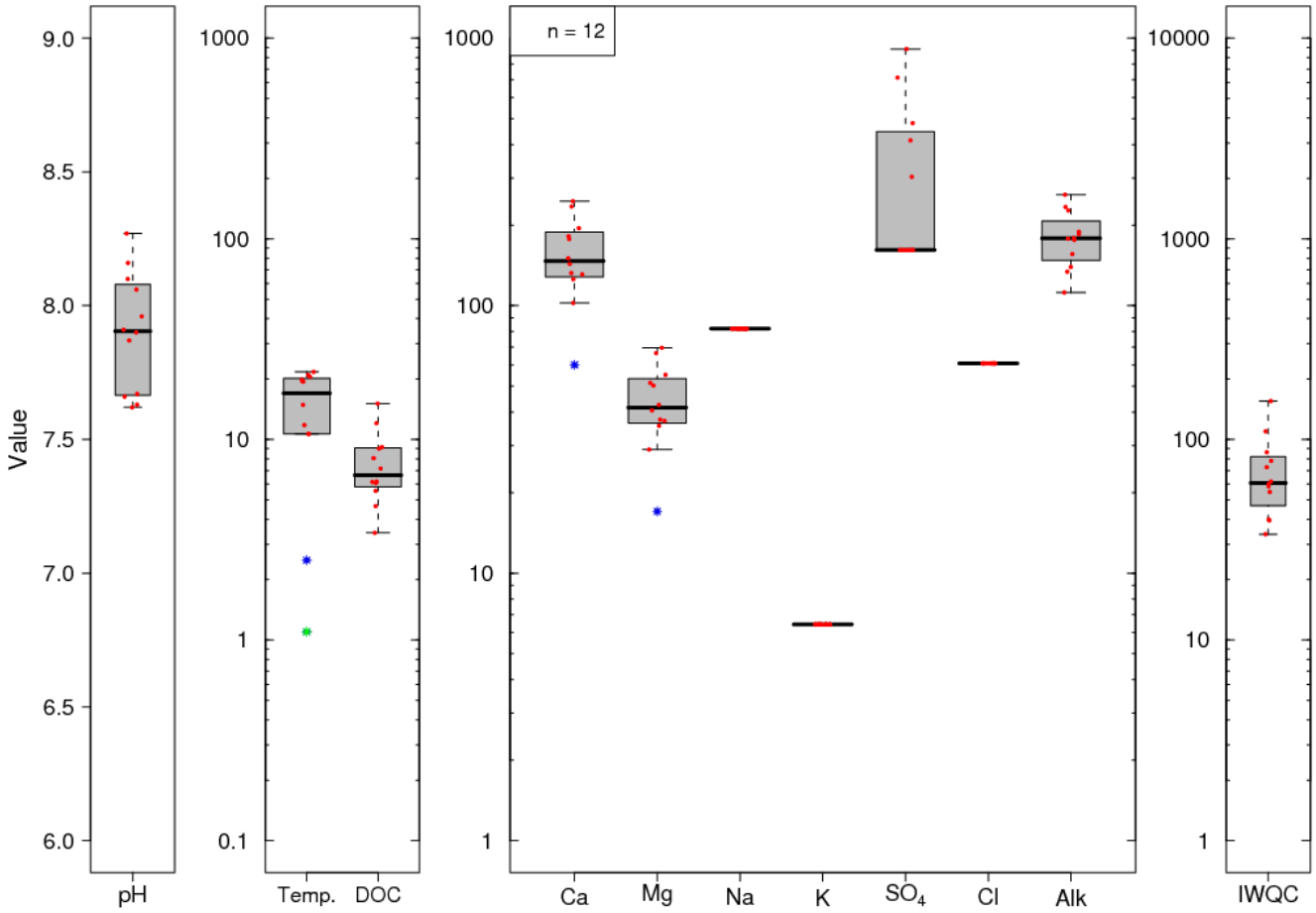

Figure 19. Box and whisker plot of BLM inputs and BLM IWQC for Aurora_Up.

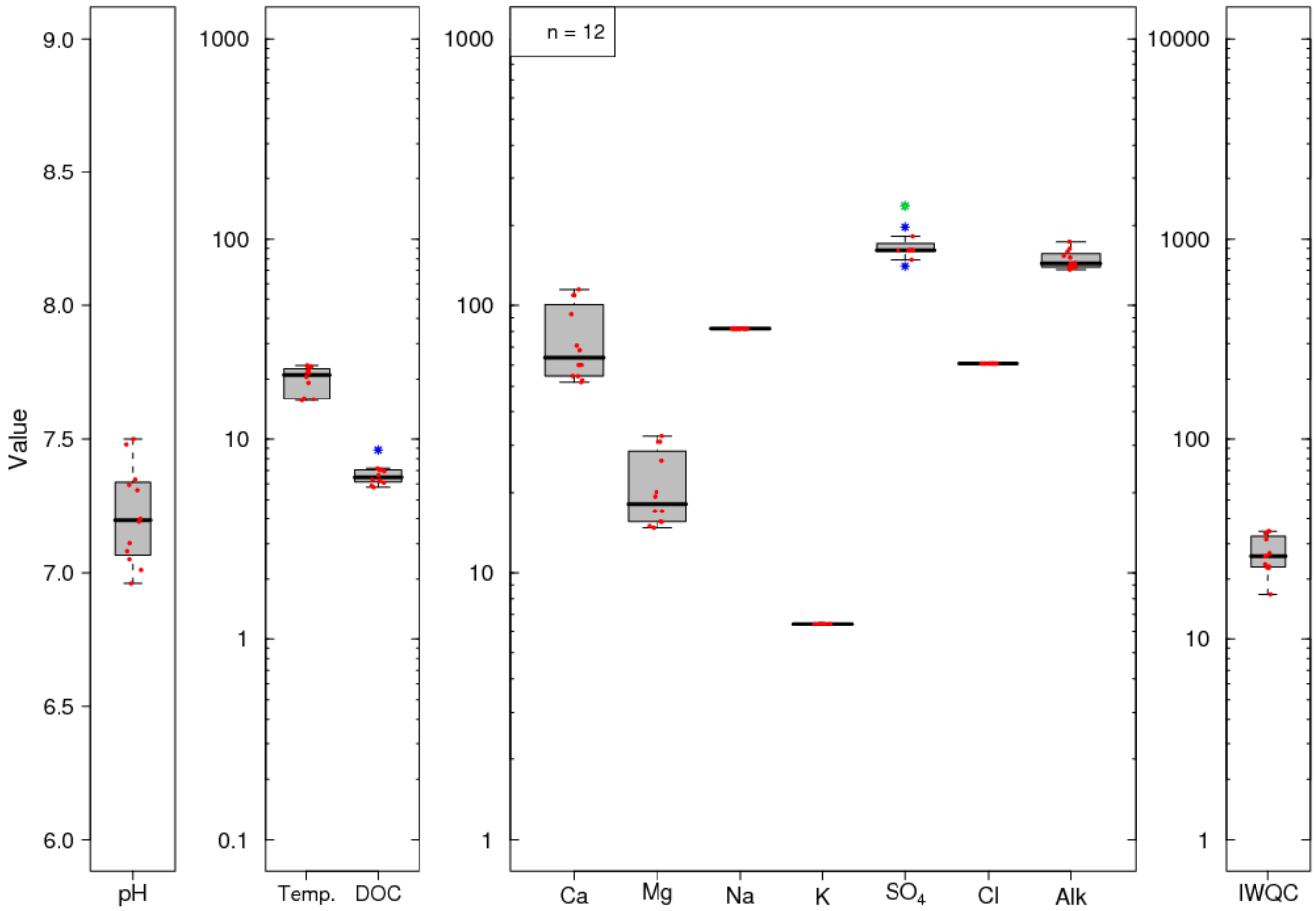

Figure 20. Box and whisker plot of BLM and BLM IWQC for Aurora_Eff.

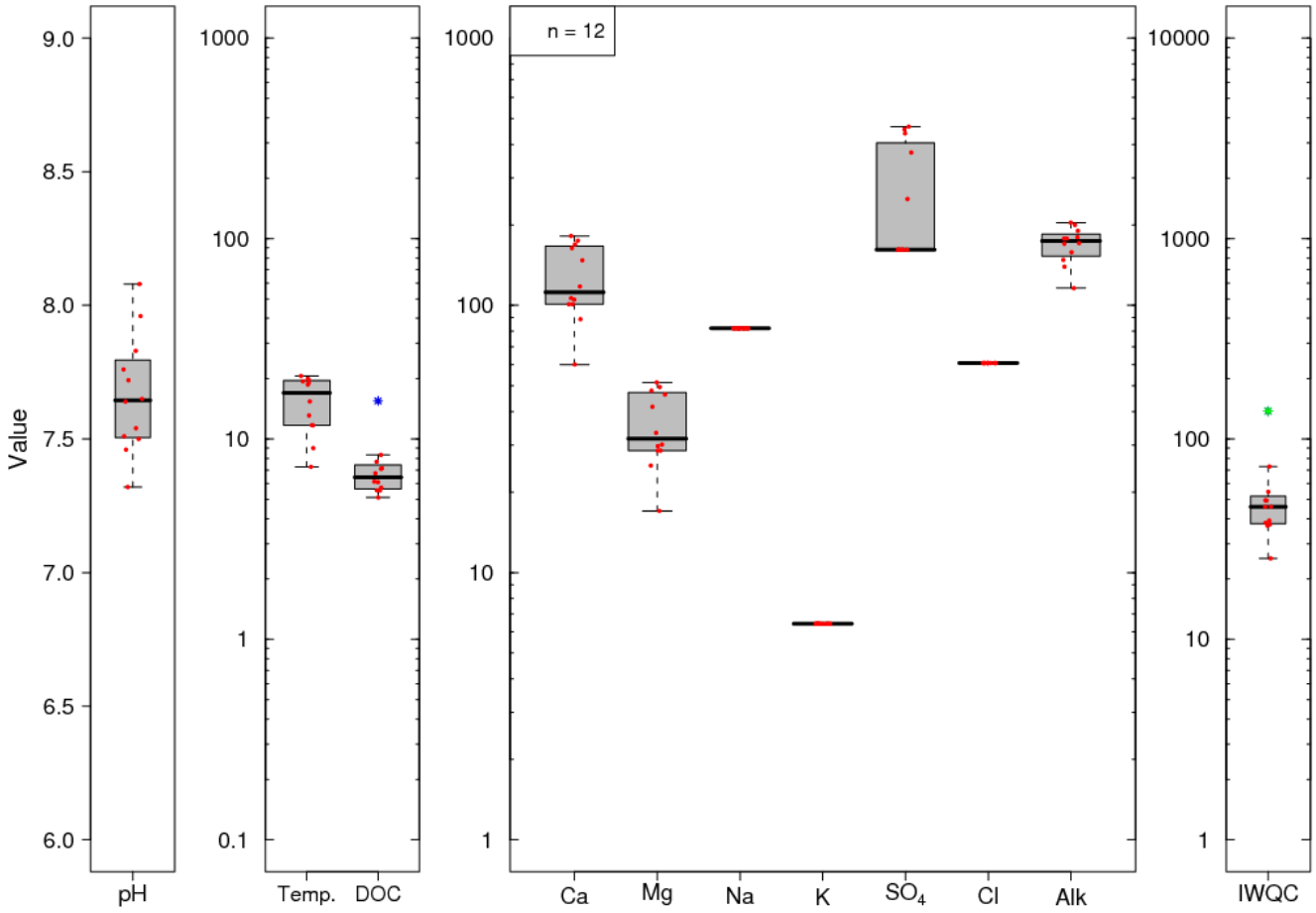

Figure 21. Box and whisker plot of BLM inputs and BLM IWQC for Aurora_Down.

Currently, water effect ratios (WER) are applied as a multiplier to the HWQC for two of the sites listed in Table 2 (Blake Beyea – personal communication). Those sites are Aurora_Down and Cent_Min_Ave, and the respective WERs are 2.6 and 2.7, resulting in adjusted HWQC (and Hardness-based FMB_a) of 129 μg/L and 54.8 μg/L, respectively. For Aurora_Down, this WER-adjusted FMB_a is much higher than the value obtained from the analysis using the BLM at Aurora_Down (52.4 μg/L), although it is lower than the BLM result for Aurora_Up (142 μg/L). We have listed the WER-adjusted criteria at the Aurora_Down site because the site-specific criteria was intended to be applied downstream of the discharge. We do not actually know that the samples used in the WER analysis were taken from near where the downstream monitoring samples at Aurora_Down were taken. The fact that the WER adjusted result is bracketed by the BLM predictions at Aurora_Up and Aurora_Down suggests that the samples used in the WER analysis may have been taken from an intermediate location, and possibly closer to Aurora_Up. The large change in water quality and BLM FMB from Aurora_Up to Aurora_Down suggests that location and timing of sample collection are critically important. It may also be the case that if one of the factors that causes the low effluent pH and reduced downstream pH is dissolved CO_2(g) concentrations that are higher than would be in equilibrium with the atmosphere, than samples taken for toxicity tests used to develop a WER at this site may experience considerable pH drift as the CO_2(g) de-gasses. This pH drift up would result in reduced copper toxicity in the test samples, relative to the site-water. However, the pH of the site water would be more important for determining the bioavailability of copper to organisms exposed in the discharge. For Cent_Min_Ave, both the WER-adjusted FMB_a (54.9 μg/L) and the BLM FMB_a (46.5 μg/L) are considerably higher than the hardness equation result (20.3 μg/L). When comparing the BLM results with both of the available WER values, it is likely that these two different methods were determined using completely different samples, taken at different times and possibly from somewhat different locations.

Since the BLM-based approach incorporates the simultaneous time variability in the IWQC and in-stream Cu, by using TU values, it accounts for any correlation between the IWQC and in-stream Cu concentrations. In cases where the IWQC and in-stream Cu concentrations are positively correlated, the standard deviation of the log transformed TU values will be relatively low, and conversely, when the IWQC and in-stream Cu concentrations are negatively correlated, the standard deviation of the log transformed TU values will be relatively high.

It may also be important to investigate the sensitivity of the BLM-based probability approach to extreme values and uncertainty in measured in-stream Cu concentrations. One case in particular illustrated the important effect of an uncharacteristically high in-stream Cu concentration on the resulting FMB_a value. This case is for DEH-N25E, where one TU value was greater than 1, while the rest were below 0.3. The resulting FMB_a for this site was 32.6 μg/L (Table 2 and Appendix H7), but when the highest and lowest in-stream Cu values were removed from the analysis (the lowest and highest points were removed in order to preserve the median), the resulting FMB_a was 62.4 μg/L. There were no other cases, where this effect was so extreme, but it does illustrate that this

approach can be influence by seemingly uncharacteristic values, and it suggests that the sensitivity of the approach should be examined. In this case as a result of the one extreme copper value neither the copper concentrations nor the TU distribution were well described by a log-normal distribution. A goodness of fit statistic may be an appropriate diagnostic for cases like this in subsequent analyses.

Calculation of Chronic FMB (FMB_c)

The approach described above for the calculation of IWQC-based and HWQC-based FMB_a can be easily modified for the calculation of chronic FMB (FMB_c). The first step is to modify the IWQC, which is analogous to the criteria maximum concentration (CMC) described in the guidelines (Stephan et al. 1985), to be representative of the criteria continuous concentration (CCC). Given this, the IWQC is calculated as:

$$IWQC = CMC = \frac{FAV}{2}, \qquad \text{Eqn. 7}$$

where *FAV* is the final acute value, defined in the guidelines as the 5th percentile of the species sensitivity distribution. In order to convert the IWQC to a chronic IWQC ($IWQC_c$), the acute to chronic ratio (ACR) is applied:

$$IWQC_c = CCC = \frac{FAV}{ACR} = \frac{IWQC * 2}{ACR}. \qquad \text{Eqn. 8}$$

The next step is to convert the log standard deviations from the grab sample in-stream Cu and TU distributions to log standard deviations that are representative of 4-day averages. To do this, an effective sample size (n_e) is calculated as described in (U.S. EPA 1985b):

$$n_e = \frac{n^2(1-\rho)^2}{n(1-\rho^2) - 2\rho(1-\rho^n)}, \qquad \text{Eqn. 9}$$

where n = number of days over which the values are averaged (i.e. $n = 4$, since this is a 4-day average), and ρ is the serial correlation coefficient. For these calculations, ρ is set to 0.8, which is a reasonable assumption for relatively small streams (Charles Delos – personal communication). Once n_e is calculated, the 4-day average log standard deviations can be calculated from the original log standard deviations of the in-stream Cu and TU data (U.S. EPA 1985b):

$$s_{Cu,4-d} = \sqrt{\ln\left(1 + \frac{(\exp(s_{Cu}^2) - 1)}{n_e}\right)}, \qquad \text{Eqn. 10}$$

and,

$$s_{TU,4-d} = \sqrt{\ln\left(1 + \frac{(\exp(s_{TU}^2) - 1)}{n_e}\right)}. \qquad \text{Eqn. 11}$$

Once the log standard deviations are calculated for the 4-day average distributions, the calculation is analogous to the procedure used to calculate the FMB_a. The log standard deviations for the 4-day average scenario are substituted into the original equations, such that the 4-day average TU at the EF is:

$$TU_{4-d,EF} = 10^{[Z_{EF} * s_{TU,4-d} + \log_{10}(TU_{Median})]}, \qquad \text{Eqn. 12}$$

and the adjustment factor for the 4-day average scenario becomes:

$$AF = \frac{1}{TU_{4-d,EF}}, \qquad \text{Eqn. 13}$$

which can be used to calculate a 4-day average Cu distribution that is in compliance, so that the chronic FMB (FMB_c) is given by:

$$FMB_c = 10^{[Z_{EF} * s_{Cu,4-d} + \log_{10}(Cu_{Median,4-d,comp})]}, \qquad \text{Eqn. 14}$$

where $Cu_{Median,4\text{-}d,comp}$ is the median of the compliant 4-d average Cu distribution. These equations were used to calculate the FMB_c for both the BLM-based and hardness-based approaches, and the results are summarized in Tables 4 and 5. The results are qualitatively similar to the FMB_a results, but the magnitudes of the FMB_c values are appropriately smaller. Figure 22 is a graphical representation of the procedure, using the BLM-based approach for the Cent_Min_Ave site from the South Platte River. In panel A, the distributions are shown for the original in-stream Cu and TU grab samples (red and green lines, respectively). The distributions for the 4-day average scenarios are also shown for the in-stream Cu and TU data (purple and orange lines, respectively). As expected, the 4-day average distributions have a lower slope relative to the original grab sample distributions. This is because the variability in 4-day averages will be lower than the variability in grab samples, and hence the log standard deviations for the 4-day average scenarios are lower than the log standard deviations for the grab samples. With the distributions that are representative of the 4-day average scenarios, the procedure is identical to that described above for the calculation of FMB_a. Panel B (Figure 22) shows that the AF is 1.1, and panel C shows the revised distribution, with an FMB_c = 29 µg/L. Panel D shows the revised in-stream distributions for both the grab sample and the 4-day average scenarios, indicating that the FMB_a is higher than the FMB_c, and the FMB_c has a lower slope, as expected. Results of the same procedure are shown for the DEH-N14 South Platte River site in Figure 23. For DEH-N14, the AF is 2.3 and the resulting FMBc = 35.4 µg/L. When the hardness-based approach is used, the FMBc is simply the chronic

HWQC, as can be seen for the Cent_Min_Ave (Figure 24) and DEH-N14 (Figure 25) sites.

Table 4. Results of the probability method to calculate chronic FMB using both the BLM-based IWQC and hardness-based HWQC. Results are for site waters. To calculate the HWQC, the hardness equation was applied to the mean hardness for a given BLM data set, providing constant HWQC. If a water effect ratio (WER) was available for a given location, the site specific criterion obtained by adjusting the hardness equation results is provided in the column labeled HWQC*WER. The summary statistics used to calculate the FMBc with the BLM-based IWQC can be viewed in Appendix C.

					BLM IWQC Method		Hardness Equation Method	
River System	Station ID	Location	n	Cu Median (ug/L)	IWQC Median (ug/L)	Cu FMB_c (ug/L)	HWQC (ug/L)	HWQC*WER (ug/L)
Monument	Baptist	Baptist Rd.	49	2.55	18.6	45.7	8.1	
Monument	North_gate	Northgate Blvd.	21	2.62	19.9	37.4	9.7	
Sand_Creek	Aurora_Down	39° 45.667' N 105° 51.950' W	12	2.43	29.8	32.3	30.8	80.1*
Sand_Creek	Aurora_Up	39° 45.417' N 105° 50.817' W	12	1.34	40.1	82.5	30.8	
South_Platte	River_Down	39° 59.633' N 104° 49.552' W	24	5.42	26.0	18.8	18.1	
South_Platte	River_Up	39° 59.528' N 104° 49.709' W	26	5.86	27.8	23.7	18.6	
South_Platte	Cent_Min_Ave	39° 34.917' N 105° 01.867' W	35	2.97	31.7	29.0	12.6	34.0**
South_Platte	DEH-N14	39° 44.312' N 105° 01.083' W	17	2.46	23.4	35.4	21.1	
South_Platte	DEH-N25E	39° 45.274' N 105° 00.511' W	17	2.42	31.1	20.8	20.8	
South_Platte	DEH-N38	39° 46.155' N 104° 58.996' W	17	2.64	33.7	10.6	22.6	
South_Platte	DEH-N46	39° 47.030' N 104° 58.524' W	17	2.77	43.6	25.7	22.0	
South_Platte	S_Adams_Up	39° 52.457' N 104° 54.815' W	33	1.23	25.4	109.0	18.2	

* WER for Aurora_Down is 2.6
** WER for Cent_Min_Ave is 2.7
BLM = Biotic Ligand Model
IWQC = BLM-based Instantaneous Water Quality Criteria
FMB_a = Acute Fixed Site Criterion
HWQC = Hardness-based Water Quality Criteria
WER = Water Effect Ratio

Table 5. Results of the probability method to calculate chronic FMB using both the BLM-based IWQC and hardness-based HWQC. Results are for effluents. To calculate the HWQC, the hardness equation was applied to the mean hardness for a given BLM data set, providing constant HWQC.

					BLM IWQC Method		Hardness Equation Method
River System	Station ID	Location	n	Cu Median (ug/L)	IWQC Median (ug/L)	Cu FMB_c (ug/L)	HWQC (ug/L)
Cache_la_Poudre	Drake	Drake WRF	3	10.2	23.9	6.0	15.8
Cache_la_Poudre	Mulberry	Mulberry WRF	3	7.19	35.5	7.2	15.8
Sand_Creek	Aurora_Eff	39° 45.683' N 105° 51.283' W	12	3.68	16.3	13.0	21.6
South_Platte	Effluent	39° 59.558' N 104° 49.619' W	26	7.05	20.8	23.5	13.5
South_Platte	MG_Effluent	39° 33.417' N 105° 02.117' W	35	13.4	31.2	28.5	15.4
South_Platte	Effluent	39° 42.350' N 104° 56.167' W	25	5.44	27.1	42.3	13.4
South_Platte	S_Adams_Eff	39° 52.443' N 104° 54.746' W	31	18.5	57.0	39.8	24.3

BLM = Biotic Ligand Model
IWQC = BLM-based Instantaneous Water Quality Criteria
FMB_a = Acute Fixed Site Criterion
HWQC = Hardness-based Water Quality Criteria
WER = Water Effect Ratio

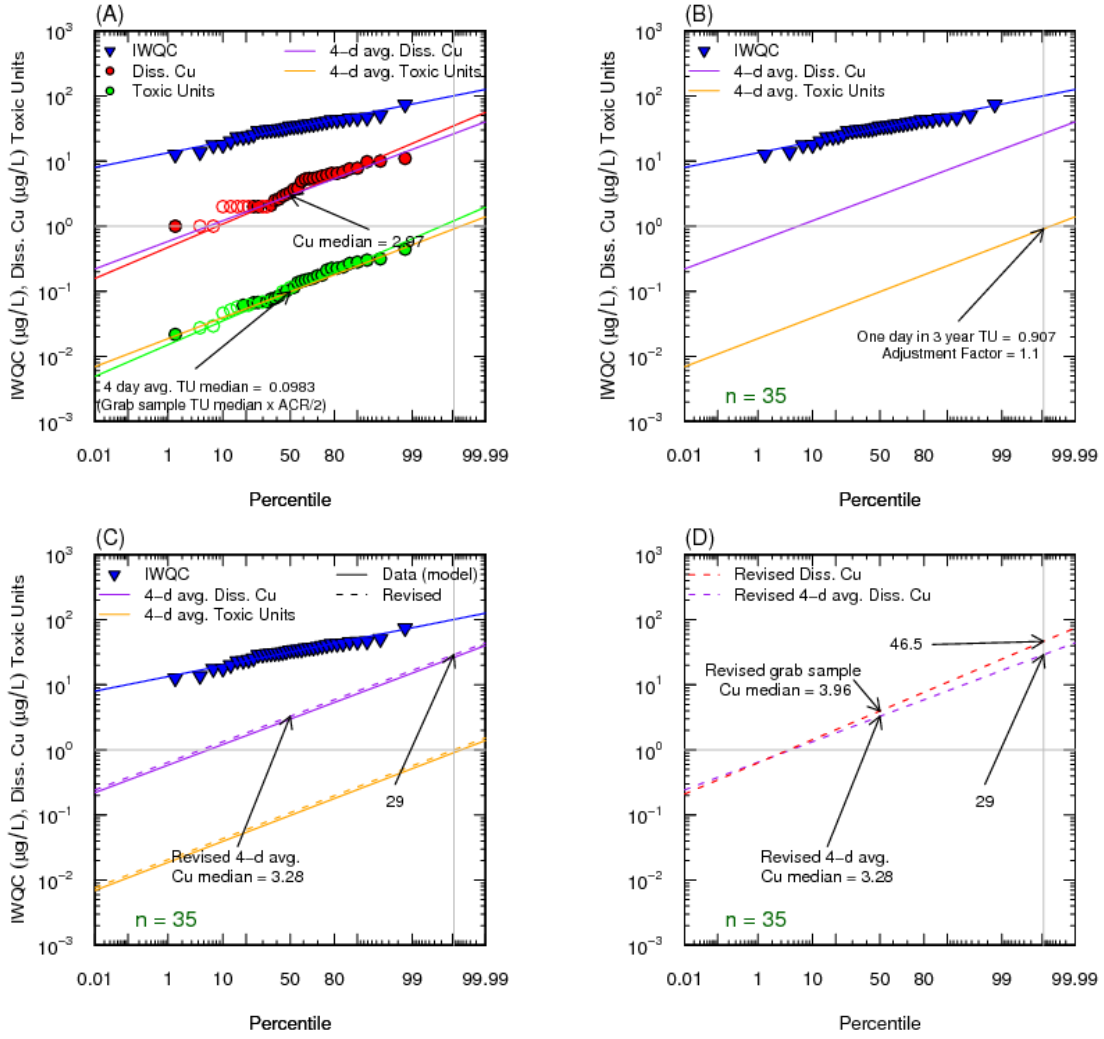

Figure 22. Graphical representation of the calculation of chronic FMB (FMBc) for the 4 day average scenario with Cent_Min_Ave South Platte River site, using chronic BLM-base IWQC. The grab sample and 4-day average distributions are shown in (A). The AF is provided in (B), and the resulting FMBc is given in (C). For comparison, the revised in-stream Cu distributions for the grab sample and 4-day average scenarios are shown in (D).

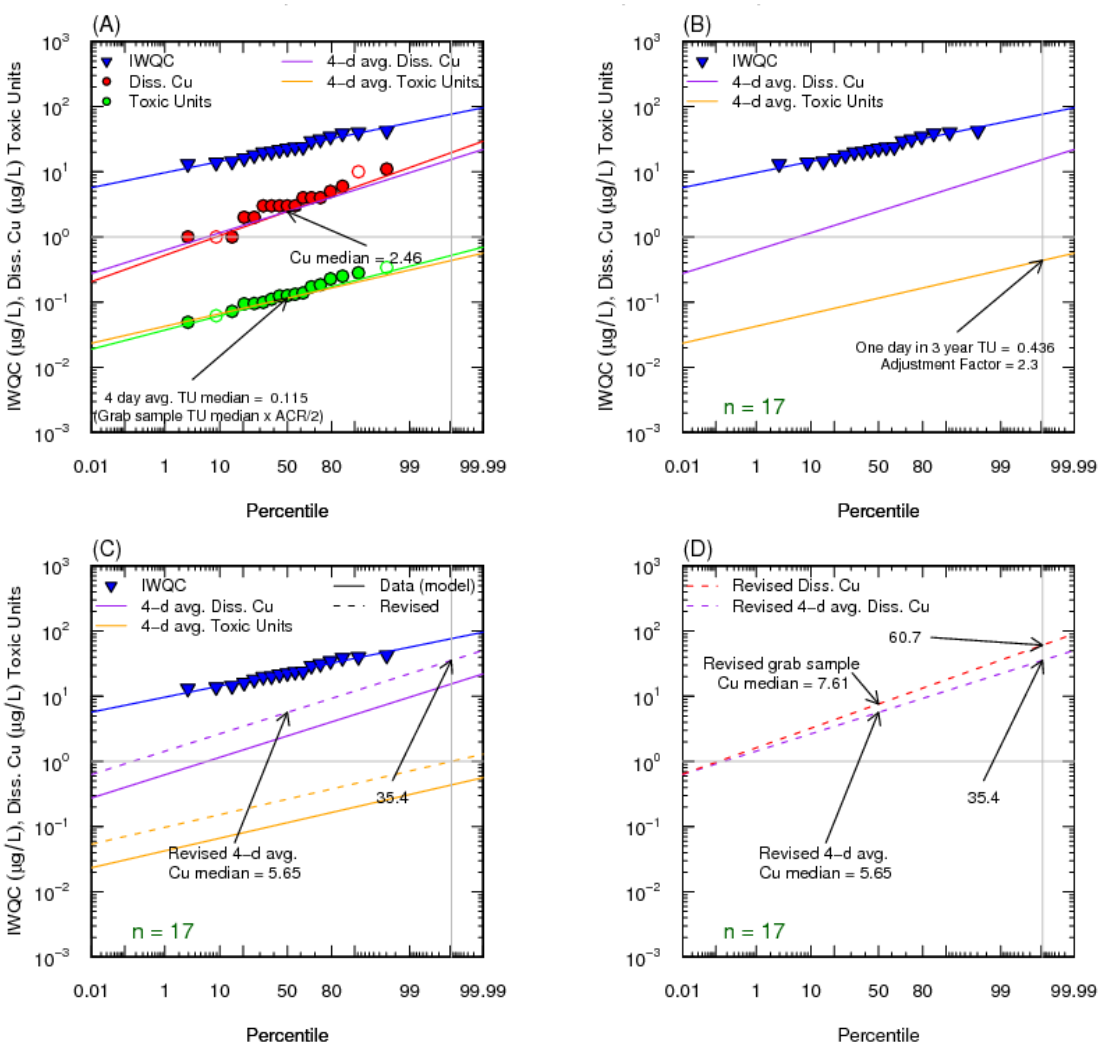

Figure 23. Graphic representation of the calculation of chronic FMB for the 4 day average scenario with DEH-N14 South Platte River site, using chronic BLM-based IWQC. The grab sample and 4-day average distributions are shown in (A). The AF is provided in (B), and the resulting FMBc is given in (C). For comparison, the revised in-stream Cu distributions for the grab sample and 4-day average scenarios are shown in (D).

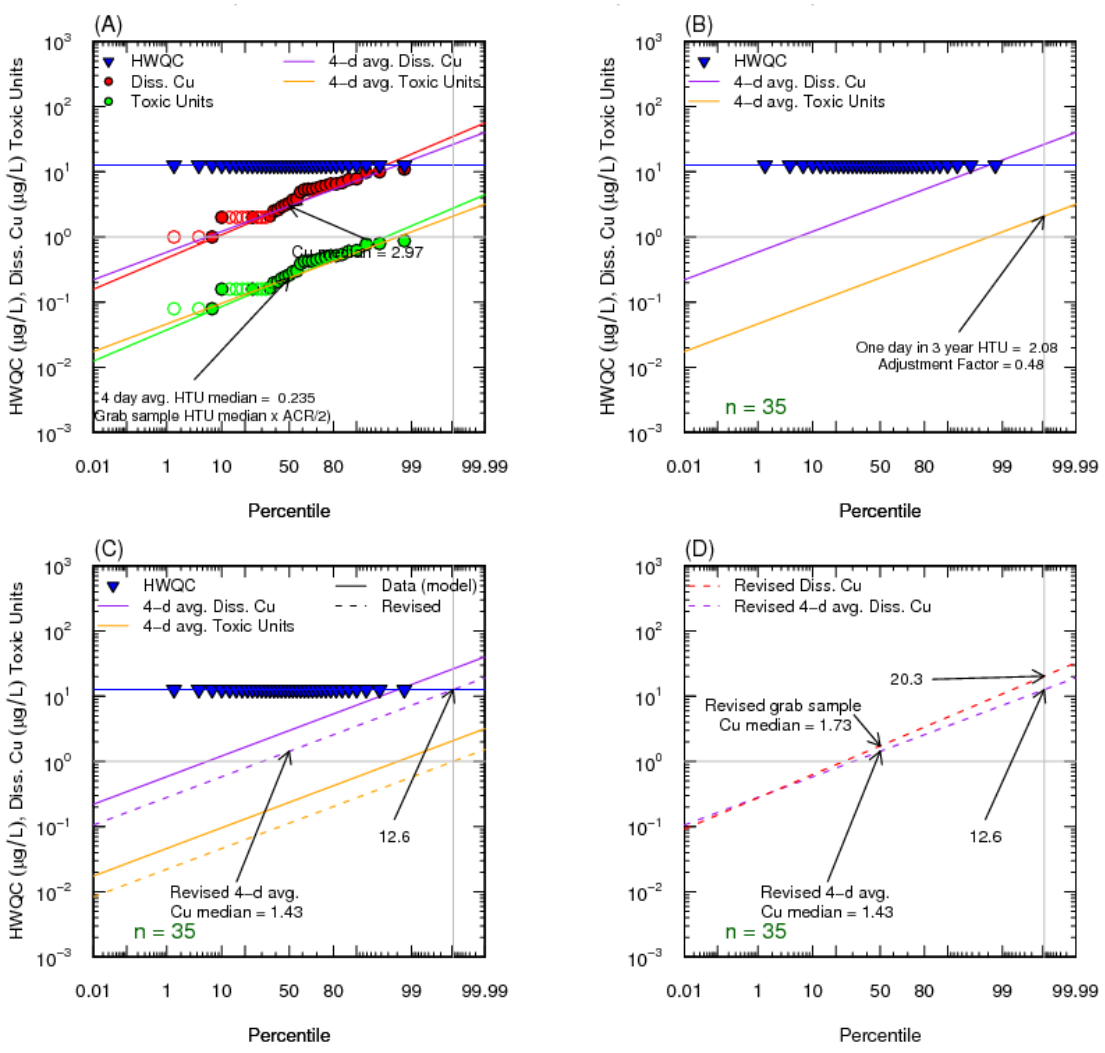

Figure 24. Example graphical representation of calculation of chronic FMB for the 4 day average scenario with Cent_Min_Ave site, using the chronic hardness-based HWQC. The grab sample and 4-day average distributions are shown in (A). The AF is provided in (B), and the resulting FMBc is given in (C). For comparison, the revised in-stream Cu distributions for the grab sample and 4-day average scenarios are shown in (D).

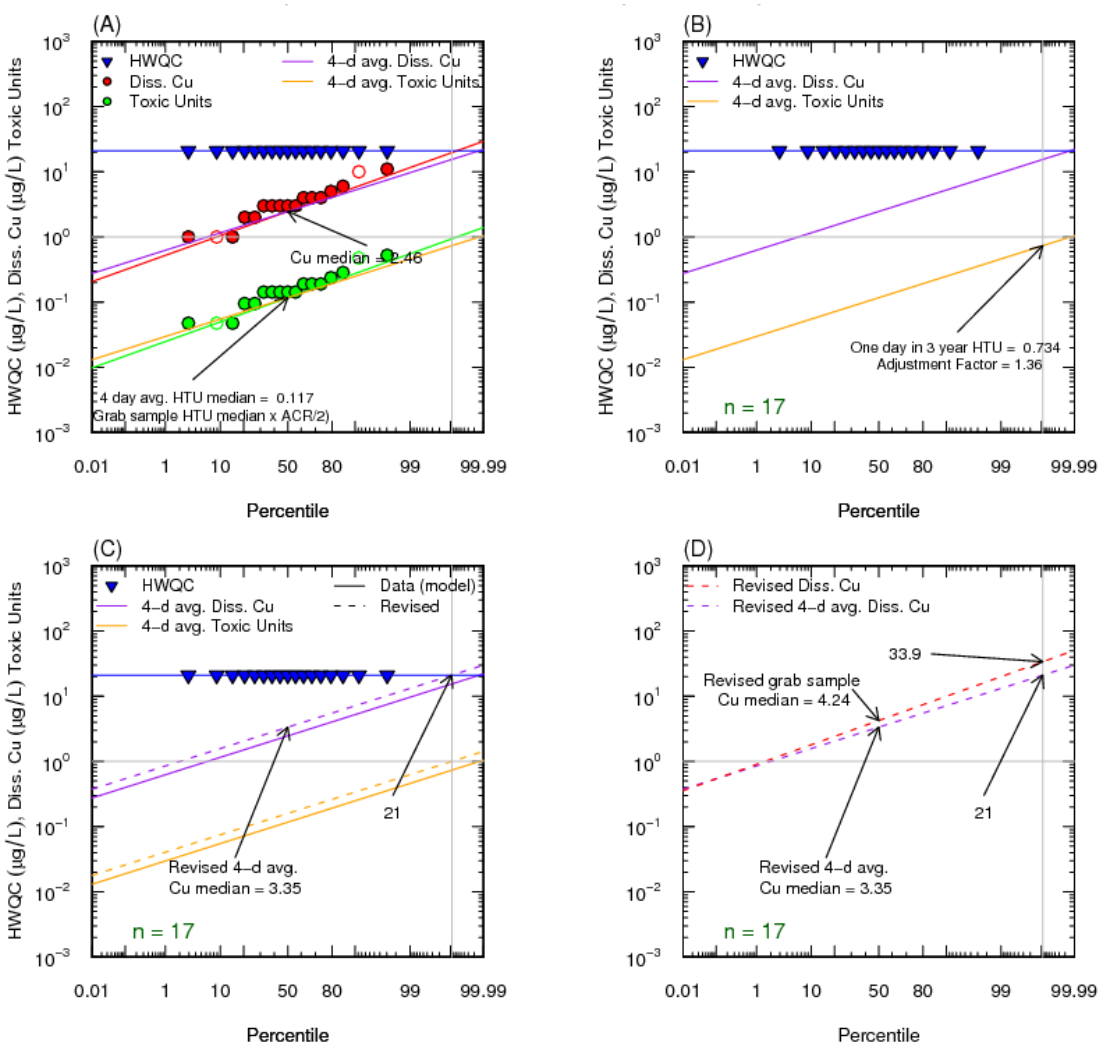

Figure 25. Example graphical representation of the calculated chronic FMB for the 4 day average scenario with DEH-N14 South Platte River site using the chronic hardness-based HWQC. The grab sample and 4-day average distributions are shown in (A). The AF is provided in (B), and the resulting FMBc is given in (C). For comparison, the revised in-stream Cu distributions for the grab sample and 4-day average scenarios are shown in (D).

Summary

The BLM was used to develop fixed monitoring benchmark (FMB) at twelve sites in the state of Colorado. At these locations the water quality parameters used by the BLM typically varied over time, and as a result the BLM WQC was also time-variable. The time variability of the BLM results can be analyzed using a probability-based method to develop a fixed criterion value. A similar approach can be applied to develop a chronic FMB by considering the effect of four day averaging on variability of the TU distribution. The use of these methods to develop fixed acute and chronic WQC will make it easier to determine compliance in subsequent monitoring.

Although a large amount of monitoring data were examined as part of this analysis, a relatively small percentage could be used because most of the existing data were missing a critical input parameter such as pH, DOC, or dissolved copper concentrations. Sensitivity analyses at these sites suggest that these parameters should not be estimated, and as a result the probability-based analysis was restricted only to samples where these parameters were measured. Other water quality parameters were not as critical at these sites, and estimates for other parameters were used when necessary to increase the number of useable observations in the database for these sites. It is important to emphasize that measured values for all parameters are preferred, and that a sensitivity analysis performed with data from a different site might give different results. The results in this document, therefore, should not be used as a rationale for not measuring cation and anion concentrations at other sites.

Application of the BLM and development of FMB values at these twelve sites in CO shows that the BLM typically predicts higher FMB than the hardness equation. Where WER information is available, the BLM FMB is consistent with the values obtained from the WER. However, comparison of these two methods is made somewhat more difficult by the fact that the two results are based on different samples taken at different times, and probably different locations.

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Appendices

Appendix A. Colorado Rivers Data Availability

Table A1. Summary of data availability. R indicates that measurements were reported for the constituent of interest, and (R) indicates that measurements were available, but that reported values are below detection.

System	Agency	Site	Total observations	Useable observations	T	pH	DOC	Ca	Mg	Na	K	Alkalinity	Cu
South Platte	Aurora	Aurora_Up	88	12	R	R	R					R	R
		Aurora_Eff	89	12	R	R	R					R	R
		Aurora_Down	89	12	R	R	R					R	R
	Big Dry Creek	bdc0.1	2	0	R	R							R
		bdc0.5	62	0	R	R		R	R	R		R	R
		bdc1.0	72	0	R	R		R	R	R		R	R
		bdc1.5	70	0	R	R		R	R	R		R	R
		bdc10.0	72	0	R	R		R	R	R		R	R
		bdc15.0	72	0	R	R		R	R	R		R	R
		bdc12.0	3	0	R	R		R	R	R		R	R
		bdc2.0	72	0	R	R		R	R	R		R	R
		bdc3.0	72	0	R	R		R	R	R		R	R
		bdc4.0	72	0	R	R		R	R	R		R	R
		bdc5.0	72	0	R	R		R	R	R		R	R
		bdc6.0	71	0	R	R		R	R	R		R	R
	Brighton	Effluent	29	0	R	R	R					R	
		River_Down	57	0	R	R	R					R	
		River_Up	57	0	R	R	R					R	
	Centennial	Upstream	135	0	R	R	R					R	(R)
		Mint_Ave	130	35	R	R	R					R	R
		MG_Effluent	102	35	R	R	R					R	R
	Conoco	River_Down	22	0	R	R							R
		River_Up	24	0	R	R							R
	DEH	DEH-14	26	16	R	R	R	R	R	R	R		R
		DEH-N25E	26	17	R	R	R	R	R	R	R		R
		DEH-N38	26	17	R	R	R	R	R	R	R		R
		DEH-N46	26	17	R	R	R	R	R	R	R		R
	Glendale	Colo_Blvd	65	2	R	R	R					R	R
		Effluent	70	12	R	R	R					R	R
		Gendale_USGS	66	0	R	R	R					R	R
	Littleton-Engelwood	Bear_Cr_Bike_Br	6	0		R							
		Bear_Cr_Sheridan_USGS_Gauge	70	0	R	R						R	R
		Big_Dry_Cr_Littleton	92	0		R							
		Creek_S_PSC/Xcel	24	0	R	R							
		Harvard_Gulch	30	0	R	R							
		LE_Effluent	167	0	R	R						R	R
		Little_Dry_Cr_Englewood	103	0	R	R							
		PSC/Xcel_Effluent	93	0	R	R							R
		SPR_Dartmouth_Ave	167	0	R	R							R

System	Agency	Site	Total observations	Useable observations	T	pH	DOC	Ca	Mg	Na	K	Alkalinity	Cu
		SPR_Engelwood_GC	41	0	R	R							
		SPR_Evans_Ave	167	0	R	R						R	R
	MWRD	Burling_Diotch_64th_Ave	60	0	R	R						R	R
		Clear_Cr_York_St	48	0	R	R						R	R
		S_Platte_100_Up_Clear_Cr	137	0	R	R						R	R
		S_Platte_124th_Ave	146	0	R	R						R	R
		S_Platte_160th_Ave	89	0	R	R						R	R
		S_Platte_64th_Ave	139	0	R	R						R	R
		S_Platte_78th_Ave	139	0	R	R						R	R
		S_Platte_88th_Ave	139	0	R	R						R	R
		S_Platte_Co_Rd_18	47	0	R	R						R	R
		S_Platte_Co_Rd_28	47	0	R	R						R	R
		S_Platte_Co_Rd_8	47	0	R	R						R	R
		S_Platte_Hwy_52	68	0	R	R						R	R
		S_Platte_McKay_Rd	21	0	R	R						R	R
		Sand_Cr_Burlington_Ditch_Flume	125	0	R	R						R	R
	South Adams	S_Adams_Eff	88	0	R	R	R	R		R		R	
		S_Adams_Up	110	14	R	R	R	R	R	R	R	R	R
	Thornton	Clear_Ck_Derby_Gage	32	0	R	R						R	
		SoPlatte_Burl_Canal	32	0	R	R						R	
		SoPlatte_Up_Clear_Ck	32	0	R	R						R	
	Urban Drainage	19th_Ave_14	59	0		R	R					R	R
		Henderson_15	58	0		R	R					R	R
		Sand_Cr_15a	54	0		R	R					R	R
		Toll_Gate_16a	35	0		R	R					R	R
		Union_14	49	0		R	R					R	R
Boulder	Unknown	BC-107	31	0	R	R	R	R	R	R	R	R	
		BC-95	31	0	R	R	R	R	R	R	R	R	
		BC-aWWTP	30	0	R	R	R	R	R	R	R	R	
Cache la Poudre	Unknown	Mulberry	22	3	R	R	R	R	R	R	R	R	R
		Drake	27	3	R	R	R	R	R	R	R	R	R
Fountain	Unknown	Up_SSD1	40	0	R	R	R	R	R	R	R	R	
		Up_SSD2	20	0	R	R	R	R	R	R	R	R	
		Up_Pk_Tr	20	0	R	R	R	R	R	R	R	R	
		Twin_Bridges	2	0	R	R	R	R	R	R	R	R	
Monument	Unknown	Baptist	49	49	R	R	R	R	R	R	R	R	(R)
		North_Gate	21	21	R	R	R	R	R	R	R	R	(R)
		Woodman	21	0	R	R	R	R	R	R	R	R	(R)
Totals			***4914***	***277***									

Appendix B. Summary statistics from the BLM-based Acute Fixed monitoring benchmark (FMB_a) calculations

Table B1. Summary statistics used in the BLM-based calculation of FMB_a for site waters from the Colorado Rivers data set.

River System	Station ID	n	TU Median	s_{TU}	TU_{EF}	AF	Cu Median (μg/L)	s_{Cu}	FMB_a (μg/L)	Spearmans ρ (p-value)
Monument	Baptist	49	0.0104	0.547	0.528	1.9	2.55	0.4	65.2	0.171 (0.686)
Monument	North_gate	21	0.0382	0.189	0.148	6.73	2.62	0.2	59.2	0.5 (1)
Sand_Creek	Aurora_Down	12	0.0499	0.367	0.694	1.44	2.43	0.4	52.4	-0.0788 (0.838)
Sand_Creek	Aurora_Up	12	0.0185	0.351	0.229	4.37	1.34	0.4	142.0	0.314 (0.564)
South_Platte	River_Down	24	0.13	0.2	0.546	1.83	5.42	0.2	29.1	-0.0408 (0.85)
South_Platte	River_Up	26	0.131	0.217	0.623	1.6	5.86	0.2	37.4	0.144 (0.483)
South_Platte	Cent_Min_Ave	35	0.0611	0.35	0.751	1.33	2.97	0.3	46.5	0.233 (0.252)
South_Platte	DEH-N14	17	0.0714	0.21	0.323	3.09	2.46	0.3	60.7	0.635 (0.0111)
South_Platte	DEH-N25E	17	0.057	0.5	2.06	0.485	2.42	0.5	32.6	0.287 (0.301)
South_Platte	DEH-N38	17	0.0457	0.455	1.2	0.832	2.64	0.3	14.9	-0.303 (0.293)
South_Platte	DEH-N46	17	0.0369	0.354	0.468	2.14	2.77	0.3	38.5	0.24 (0.409)
South_Platte	S_Adams_Up	33	0.079	0.289	0.628	1.59	1.23	0.7	221.0	0.554 (0.154)

Table B2. Summary statistics used in the BLM-based calculation of FMB_a for effluents from the Colorado Rivers data set.

River System	Station ID	n	TU Median	s_{TU}	TU_{EF}	AF	Cu Median (μg/L)	s_{Cu}	FMB_a (μg/L)	Spearmans ρ (p-value)
Cache_la_Poudre	Drake	3	0.265	0.346	3.16	0.316	10.2	0.1	8.1	-0.5 (1)
Cache_la_Poudre	Mulberry	3	0.126	0.327	1.31	0.763	7.19	0.1	9.5	-1 (0.333)
Sand_Creek	Aurora_Eff	12	0.14	0.215	0.652	1.53	3.68	0.2	20.3	-0.154 (0.632)
South_Platte	Effluent	26	0.2	0.208	0.891	1.12	7.05	0.2	38.3	0.241 (0.245)
South_Platte	MG_Effluent	35	0.266	0.238	1.47	0.68	13.4	0.2	45.3	0.125 (0.474)
South_Platte	Effluent	25	0.129	0.38	1.96	0.509	5.44	0.5	71.6	0.414 (0.181)
South_Platte	S_Adams_Eff	31	0.206	0.204	0.893	1.12	18.5	0.2	61.3	-0.0921 (0.655)

Appendix C. Summary statistics from the BLM-based Chronic Fixed monitoring benchmark (FMB_c) calculations

Table C1. Summary statistics used in the BLM-based calculation of FMB_c for site waters from the Colorado Rivers data set.

River System	Station ID	Sample Type	n	TU Median	s_{TU}	TU_{EF}	AF	Cu Median (μg/L)	s_{Cu}	Cu FMB_c (μg/L)	Spearmans ρ (p-value)
Monument	Baptist	Site	49	0.0104	0.488	0.56	1.79	2.55	0.3	45.7	0.686 (49)
Monument	North_gate	Site	21	0.0382	0.167	0.204	4.91	2.62	0.1	37.4	1 (21)
Sand_Creek	Aurora_Down	Site	12	0.0499	0.325	0.829	1.21	2.43	0.3	32.3	0.838 (12)
Sand_Creek	Aurora_Up	Site	12	0.0185	0.311	0.277	3.62	1.34	0.4	82.5	0.564 (12)
South_Platte	River_Down	Site	24	0.13	0.177	0.742	1.35	5.42	0.1	18.8	0.85 (24)
South_Platte	River_Up	Site	26	0.131	0.192	0.835	1.2	5.86	0.2	23.7	0.483 (26)
South_Platte	Cent_Min_Ave	Site	35	0.0611	0.31	0.907	1.1	2.97	0.3	29.0	0.252 (35)
South_Platte	DEH-N14	Site	17	0.0714	0.186	0.436	2.3	2.46	0.3	35.4	0.0111 (17)
South_Platte	DEH-N25E	Site	17	0.057	0.446	2.25	0.444	2.42	0.4	20.8	0.301 (17)
South_Platte	DEH-N38	Site	17	0.0457	0.405	1.35	0.741	2.64	0.2	10.6	0.293 (17)
South_Platte	DEH-N46	Site	17	0.0369	0.313	0.563	1.77	2.77	0.2	25.7	0.409 (17)
South_Platte	S_Adams_Up	Site	33	0.079	0.255	0.794	1.26	1.23	0.6	109.0	0.154 (33)

Table C2. Summary statistics used in the BLM-based calculation of FMB_c for effluents from the Colorado Rivers data set.

River System	Station ID	Sample Type	n	TU Median	s_{TU}	TU_{EF}	AF	Cu Median (μg/L)	s_{Cu}	Cu FMB_c (μg/L)	Spearmans ρ (p-value)
Cache_la_Poudre	Drake	Effluent	3	0.265	0.306	3.83	0.261	10.2	0.1	6.0	1 (3)
Cache_la_Poudre	Mulberry	Effluent	3	0.126	0.289	1.61	0.62	7.19	0.1	7.2	0.333 (3)
Sand_Creek	Aurora_Eff	Effluent	12	0.14	0.189	0.875	1.14	3.68	0.2	13.0	0.632 (12)
South_Platte	Effluent	Effluent	26	0.2	0.183	1.2	0.831	7.05	0.2	23.5	0.245 (26)
South_Platte	MG_Effluent	Effluent	35	0.266	0.21	1.94	0.516	13.4	0.2	28.5	0.474 (35)
South_Platte	Effluent	Effluent	25	0.129	0.337	2.32	0.431	5.44	0.4	42.3	0.181 (25)
South_Platte	S_Adams_Eff	Effluent	31	0.206	0.18	1.21	0.828	18.5	0.1	39.8	0.655 (31)