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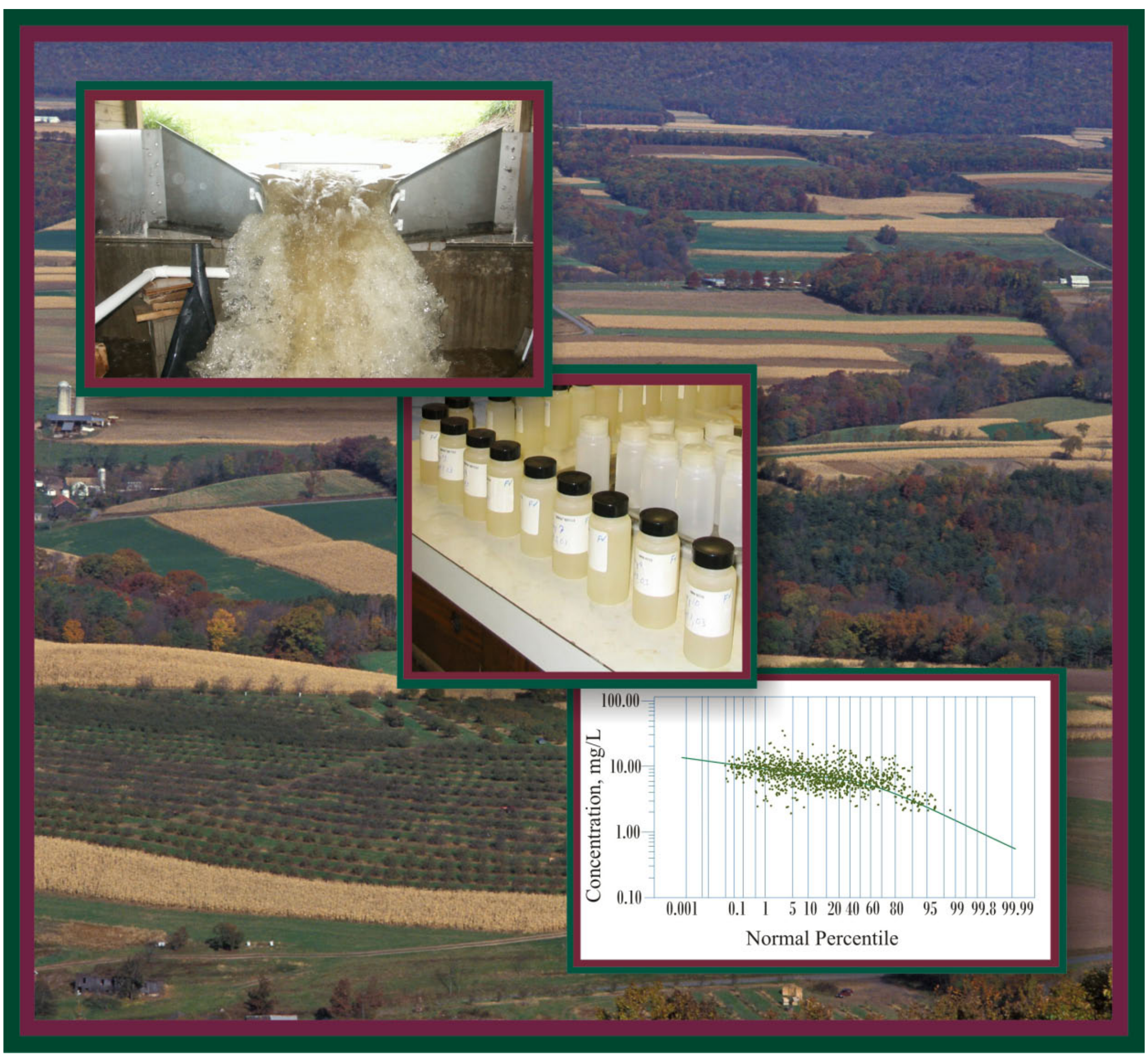

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Development of Duration-Curve Based Methods for Quantifying Variability and Change in Watershed Hydrology and Water Quality

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Foreword

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This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director
National Risk Management Research Laboratory

Abstract

During the past decades, U.S. Environmental Protection Agency (EPA), U.S. Department of Agriculture (USDA) and other Federal program administrative and regulatory agencies spent considerable amounts of time and money to manage risks to surface waters associated with agricultural activities, urbanization and other avenues of nonpoint source pollution. A variety of best management practices (BMPs) exist for this purpose and have been installed throughout the country, yet very little is known about their overall effectiveness in reducing stressors at the watershed scale. The objective of this research is to explore and develop uniform methods for simple quantification of hydrology and water quality data, focusing on watersheds containing agricultural BMPs. A significant motivation for the research is to provide tools that can be used to identify and quantify the major factors that connect watershed hydrology and water quality (such as climate, soil type, slope, land use). These connecting factors are important for evaluating the effectiveness of agricultural and other BMPs, because they often determine stream and stressor management decisions. Research methods must take into account natural variability and uncertainty in watershed response to BMP installation and precipitation events. The research project documented in this report is a collaborative effort, funded through an Interagency Agreement, between U.S. EPA's National Risk Management Laboratory and USDA's North Appalachian Experimental Watershed (NAEW) in Coshocton, OH. Project objectives were achieved through an examination of historical data collected at the NAEW, with examinations of other related databases. As a result of this research, methods were developed to quantify BMP effectiveness, and to understand how natural systems respond to watershed changes over time. The research will benefit states and other stakeholders faced with assessing the performance and effectiveness of BMPs within a watershed management framework.

Keywords: Best management practices, BMP, agriculture, hydrology, water quality, duration curves, effectiveness

Notice

The U.S. Environmental Protection Agency through its Office of Research and Development collaborated in the research described here. It has been subjected to the Agency`s review and has been approved for publication as an EPA document.

Table of Contents

Figures

Tables

Acknowledgements

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Introduction

Objectives and Scope

The project objective is to explore and develop uniform methods, based on the duration curve concept, for comparing hydrology and water quality data from watersheds subjected to agricultural and other best management practices (BMPs). The objective will be met using historical watershed hydrology and water quality data, which take into account risk and natural, observed variability and uncertainty in watershed response to BMPs and precipitation events.

The stated objective of the Clean Water Act is to restore and maintain the chemical, physical, and biological integrity of the Nation’s waters. What follows this statement are laudable goals and policies, but we have learned in the intervening years that clear success is often difficult to demonstrate. In part this difficulty lies with the goals of the Clean Water Act that focus on source control rather than the improvement of ambient water quality (Brady 2004). Sources of pollution, both point and nonpoint, are integrated within the boundaries of the watershed to yield an ambient water-quality condition, but are addressed separately by Clean Water Act programs. In recent years, the U.S. Environmental Protection Agency (EPA) began addressing the difference in emphasis by advocating a watershed approach (http://www.epa.gov/owow/watershed/approach.html) to managing water resources, and states followed suit via implementation of a rotating basin approach (National Research Council 2001) to monitoring. The U.S. EPA supports the watershed approach with concrete documentation regarding state monitoring programs (U.S. Environmental Protection Agency 1997, 2003, 2005), but implementation authority rests with state and local entities. Progress has also been made in monitoring technology and the centralized collection of data on the internet (see, for example U.S. EPA’s STORET database: http://www.epa.gov/storet/). It remains the case, however, that most water-resource managers do not have access to the comprehensive water quality and quantity data needed to assess changes in condition for particular watersheds with confidence.

In addition to the regulatory and administrative challenges outlined above, the challenge with acquisition of watershed-monitoring data is twofold. First, the natural science of watershed management is complex (Montgomery et al. 1995, Black 1997, Leopold 1997, National Research Council 1999). Surface-water quality at any given time is a combination of atmospheric sources (wet/dry deposition), groundwater exchange, runoff from land sources, municipal and industrial point sources, and in-stream constituents from the bed and bank material. Precipitation alters the balance of sources on daily, monthly and annual time scales. Terrestrial and aquatic ecosystems alter water quality on seasonal and annual time scales via nutrient cycling, microbial activity, primary production and other inputs of waste and organic material. In addition to temporal concerns, the size and location of a watershed will influence its response to each of these variables through climate, vegetation, slope and soil type. Second, anthropogenic sources are often unpredictable and dynamic. Both point and nonpoint sources vary according to daily, seasonal and annual time scales. Municipal water use has daily maxima, fertilizer and tillage practices contribute pollutants according to seasonal cycles, and development patterns are erratic. The project detailed in this report provides no answers to these complex questions, but it does aim to provide simple methods for interpreting monitoring data that take these variables into account.

Duration Curves

The purpose of this study is to explore and develop methods based on duration curves for quantifying change in watershed hydrology and water quality. The reader is referred to Bonta and Cleland (2003), for a more in-depth treatment of the basic concepts of duration curves. Duration curves (DCs) are plots of the percent of time that a given value of a variable, such as flow rate, is exceeded. The most widely applied type of DC is the flow duration curve (FDC). Flow duration curves have been used since the late 1800s to characterize the duration of watershed flows for a variety of water-resource purposes. Miller (1951) showed how FDCs could be combined with sediment concentration flow curves to estimate total loads of sediment for several rivers in the western United States. Searcy (1959) suggested FDCs could be used for other chemical constituents. More recently, Vogel and Fennessey (1995) outlined a variety of applications of FDCs for water resource problems, which include assessment of water quality.

Other investigators have used DCs in water quality studies to compute total yields and average load rates on an annual or period-of-interest basis (e.g., Miller 1951, Searcy 1959, Ledbetter and Gloyna 1964, Bourodimos et al. 1974, Steele et al. 1974, Sherwani and Moreau 1975, Goolsby et al. 1976, Larson et al. 1976, Lettenmaier 1977, Simmons and Heath 1979, Harned et al. 1981, Smith et al. 1982, Kircher et al. 1984, Leib et al. 1999, Bonta 2000, Bonta and Dick 2003). The calculations in these studies result in constituent distributions that are typically integrated to calculate an average concentration or load rate. However, the intermediate DCs contain information that is useful for evaluating change in condition over time and for total maximum daily load (TMDL) applications (Cleland 2003, U.S. Environmental Protection Agency 2007).

Three distinct relationships can be derived from the duration curve concept, as illustrated in Figure 1. FDCs, as described above, establish the basic relationship between flow (also called discharge) and the percent of time that a given flow is exceeded for a specific stream or river location (termed “exceedance level” in this report). High flows occur infrequently and are thus exceeded a small percent of time, while low baseflow conditions are exceeded frequently (90% and above; Cleland, 2003; U.S. Environmental Protection Agency, 2007). Concentration-duration curves (CDCs) show the concentration of a given water-quality constituent (e.g., copper, sediment) for each corresponding point on a FDC. The shape and utility of the CDC depends on the relationship between the constituent concentration and stream flow. When flow is multiplied by concentration to calculate the load for a given constituent, the resulting data may be plotted as a load duration curve (LDC); this formulation can be particularly useful in TMDL applications.

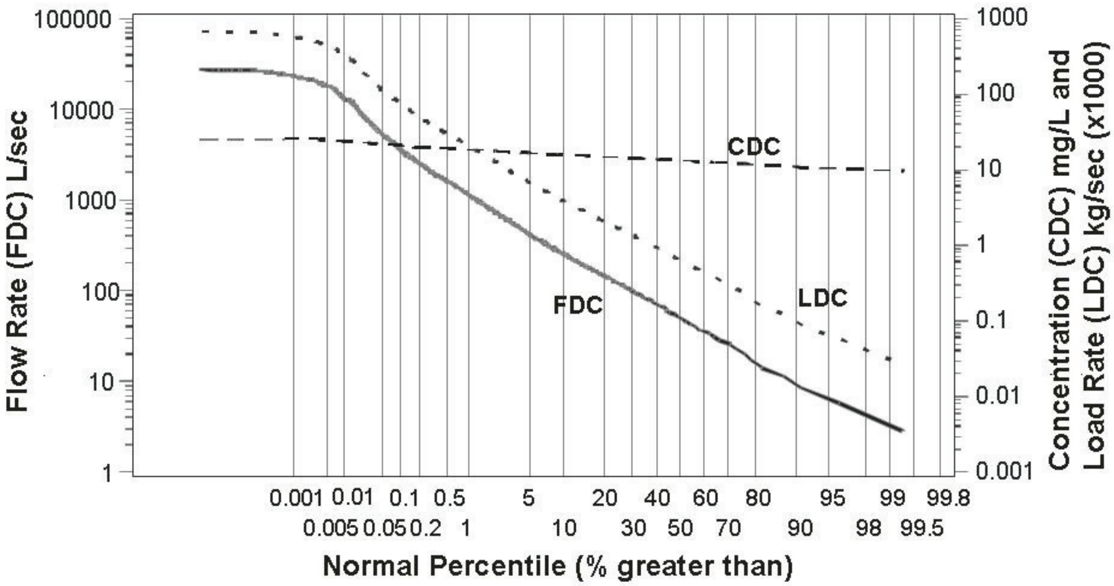

Figure 1. Example showing the relationship between flow duration curves (FDC), concentration duration curves (CDC) and load duration curves (LDC). Each is plotted as a percent of time that the condition is exceeded, yielding a graph with high flow conditions to the left (low percentile, less frequent exceedance).

Approach and Data Sources

Approach

The approach taken for the research described in the report is exploratory, empirical, and statistical. Data sets with long time periods and extensive baseflow and stormflow data for water-quality constituents are used to investigate duration-curve-based methods. Grouping of data and patterns may then be associated with land management and season of year. Regressions between flow rate and concentration are investigated for discrete samples. Examining the data in this manner will quantify variability, uncertainty and risk, and not simply average across temporal variation.

Data Sources

The primary data source used in the project report was the 7.3-km^2 Watershed WE38, a subwatershed of east Mahantango Creek (see for details Schnabel et al. 1993, Gburek and Folmar 1999, Pionke et al. 1999). Mahantango Creek is a tributary of the Susquehanna River located about 30 km north of Harrisburg, PA. WE38 is an upland agricultural watershed in the nonglaciated Appalachian Valley and Ridge Physiographic Province. Land use consists of roughly 57% cropland, 35% forest and woodlots and 8% pasture. Elevations in the watershed range from 787 to 1575 ft above sea level, and the average annual precipitation is 39.4 inches. The characteristic that makes these data valuable for analyses in this report is that they are a continuous, long-term, short-time increment stream flow data set that spans the period from 1968 through 2003. Monitoring well data, precipitation data, and water-quality data from grab samples for many constituents from 1984 through 2003 (~2500 samples) are other ideal characteristics of the data set. The data were contributed by the Pasture Systems and Watershed Management Research Unit of the USDA-Agricultural Research Service.

Other data for the project came from the North Appalachian Experimental Watershed (NAEW), which was established in 1935 in the uplands area of Coshocton County. The NAEW is a 1050-acre outdoor laboratory facility (experimental watershed) that was initiated to develop methods for the conservation of soil and water resources. The NAEW is located near the town of Coshocton in east central Ohio, an unglaciated portion of the state with rolling uplands. Underlying bedrock includes sandstone, shale, limestone, clay, and coal. Soils are medium textured and range from well-drained, with no impeding soil horizon, to soils that have a clay horizon. Average annual rainfall is 37.4 inches.

At the NAEW, historic hydrology and water quality data have been collected from small experimental watersheds that range in size from 1 to 300 acres. These data include hydrology and meteorological data collected over the last 70 years, water quality data collected over the last 25+ years, and other data with shorter records such as soil moisture. Runoff and water quality data have been collected continuously on several watersheds using a network of weather stations, rain gauges, lysimeters, automated samplers and flumes.

Constructing Duration Curves: Types and Examples

Flow Duration Curves (FDCs)

A flow duration curve is a plot of the percent of time that flow rates are exceeded, and it removes information on the sequence of recorded flows. There are two methods for developing FDCs, using average flows (e.g., average daily flow), and using short-time-increment, “instantaneous” flows (e.g., “breakpoint” data). Breakpoint data are recorded when there is a break in the slope of stage hydrograph. This is the most accurate representation of hydrograph traces. Alternatively, breakpoint data can be approximated by short sampling interval data (e.g., every 5 min). WE38 data have a 5-min sampling recording frequency. FDCs using averaged data are constructed by ranking available flow data (high to low) and using the rank position to calculate a plotting position, or exceedance probability. This is accomplished using an equation such as the following for annual data containing average daily observations (Fennessey and Vogel 1990):

$$p_i = \frac{i}{365n+1} \qquad (1)$$

where p_i is the exceedance probability or plotting position, and i is the rank number for a given number of observations 1,2,3,…,365n where n is the number of years of record for the data set. FDCs may be constructed using any number of observations, in which case the denominator would equal the total number of observations plus one. A FDC using instantaneous flow data is constructed by determining the fractions of durations of a flow (e.g., segments D4, D5, and D6 within total time, T, for flow rate Q_2 in Figure 2). This is repeated for many Q_i.

With either method, the graph is often plotted on a log-normal probability grid as shown in Figure 3 but may also be plotted using a linear percentile for the x-axis. Flow-duration curves characterize the range of flow rates for the period over which data were collected, and can change with the occurrence of persistently dry or wet periods. Annual variability, due to wet and dry years, is illustrated in Figure 3, and compared with the 40-year composite FDC for Watershed 174 at the NAEW (Bonta and Cleland 2003).

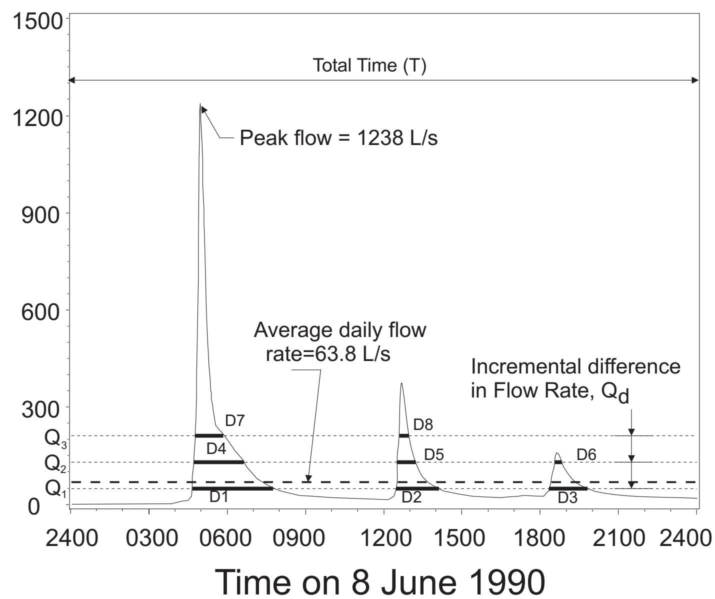

Figure 2. Hydrograph for Watershed 174, NAEW, Coshocton, OH. Figure shows how duration curves can be constructed with varying flow-rate steps, and how average daily flow rate misrepresents watershed hydrology. (Bonta and Cleland, 2003)

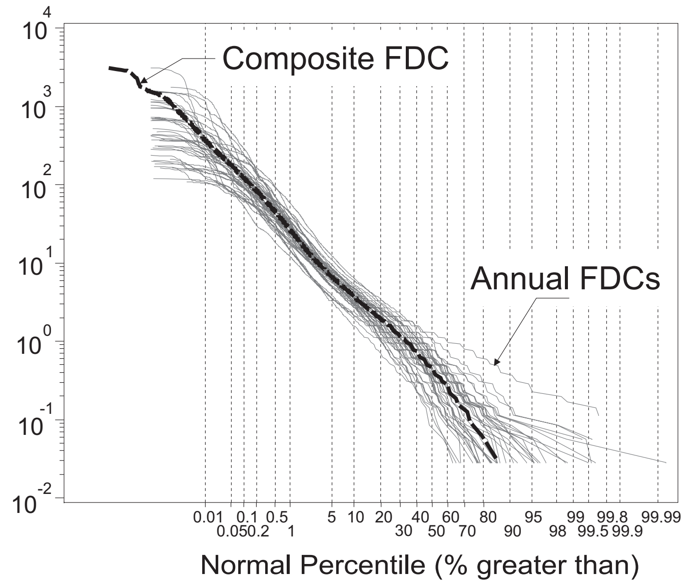

Figure 3. Variability in annual flow duration curves compared with the composite 40-year FDC for Watershed 174, NAEW, Coshocton, OH (Bonta and Cleland, 2003)

FDCs characterize a watershed's response to precipitation and other inputs, integrating multiple factors that affect stream flow at a point (topography, soil distribution, climate, land use, flow controls such as dams, etc.). A flat FDC implies a greater level of storage in the basin and a steeper FDC implies a flashy watershed, where streamflow increases quickly following precipitation. Some investigators have developed relationships between basin parameters and FDC characteristics to yield synthesized FDCs where flow data are not available (Quimpo et al. 1983, Fennessey and Vogel 1990, Franchini and Suppo 1996, Smakhtin 2001). Mathematically FDCs have the appearance of a log-normal distribution, but interpretation of them is limited due to non-independence of flow rates.

Relationships between Concentration and Discharge (regression equations)

In many watersheds a statistically-significant correlation exists between chemical concentrations (C) and flow rate (Q) (see the following for an in-depth discussion: Lewis Jr. and Grant 1979, Tasker and Granato 2000, Helsel and Hirsch 2002). Three types of linear relationships are illustrated in Figure 4. A positive trend indicates that the largest concentrations occur at high flow rates. For constituents with positive trends, the supply in the watershed is available for transport by runoff from a terrestrial source, and/or may be mobilized via in-stream sediment transport processes associated with increased stream velocities and higher flows from precipitation. A negative correlation (inverse) trend implies that constituent supply is limiting, and/or dilution occurs during precipitation events, and indicates that the largest concentrations occur at lower flow rates. Larger concentrations may occur at lower flow rates, for example, because baseflow is derived from stored water having long contact times within the aquifer, or because of continuous discharges that dominate at low flow (e.g., point sources).

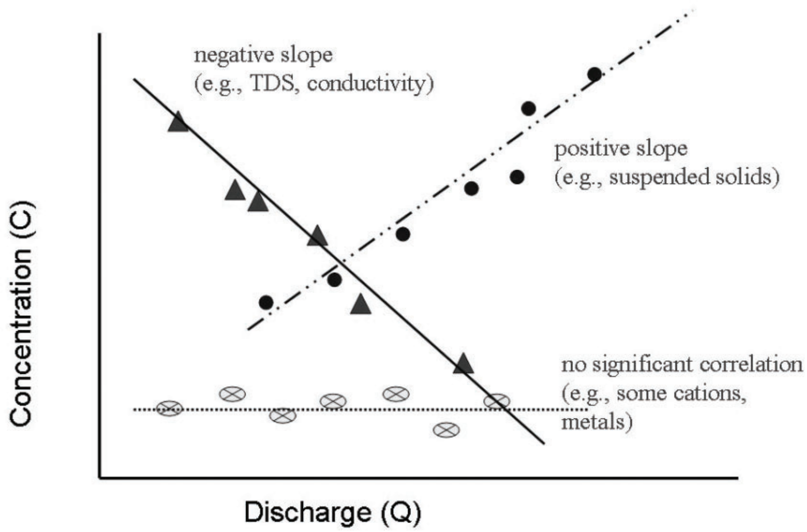

Figure 4. Three basic relationships between discharge and the concentration of a water quality constituent.

Because of possible correlations between C and Q ("C-Q regressions"), simple averages of concentrations and loads may not accurately characterize the variability of C and Q that occurs naturally, and regressions must be used. However, there is often no statistically significant correlation between C and Q, and a simple average concentration can be used to characterize the concentration for different stream flows. Incorrect use of averaging in the place of regression analysis will not allow proper estimates of water-quality-load changes when BMPs are implemented that may change either the hydrology or supply of constituents in a watershed. Smith *et al.* (1982) suggest that relations between C and Q can be related linearly, logarithmically, or inversely. These equation forms are special cases of the simple power equation,

$$C = a\,Q^{b} \qquad (2)$$

where a and b are parameters. A more general form of the power equation is

$$(C + d) = a\,(Q + e)^{b} \qquad (3)$$

where d and e are parameters that straighten a single convex or concave curve on a log-log grid. All parameters are fitted by traditional nonlinear regression techniques. Smith *et al.* (1982) also suggest a hyperbolic form

$$C = 1 / (1 + fQ) \quad (4)$$

where f is a parameter. These equations are often referred to as constituent rating curves. Relations between C and Q can exhibit much scatter, and regression confidence intervals supply a measure of uncertainty. While monotonic relations are preferred (fitting the equations given above), it is not a requirement for developing derived duration curves.

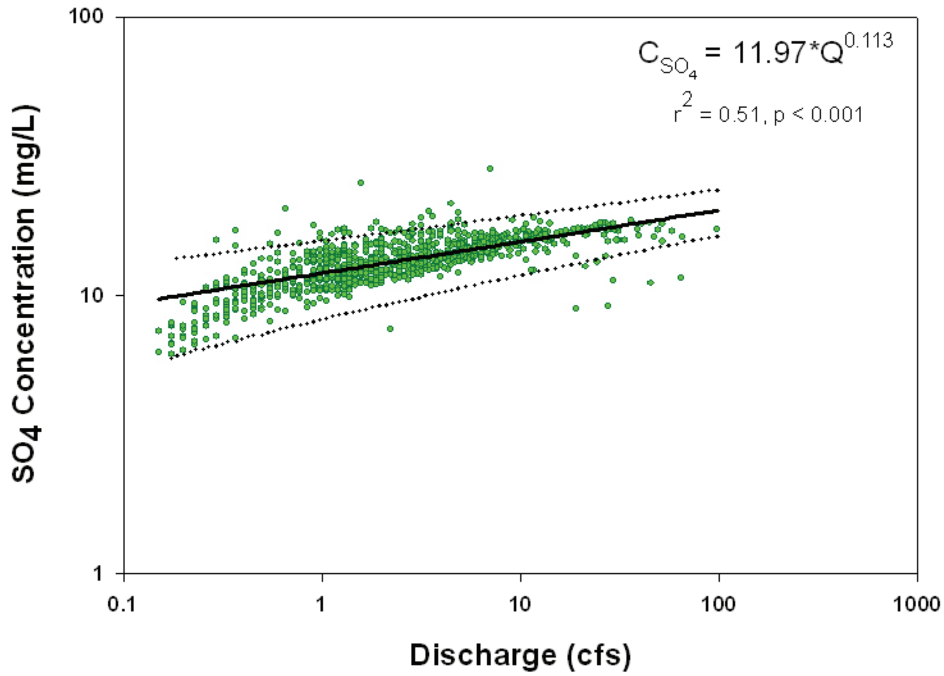

Figure 5. Plot of SO_4^{2-} concentration data versus discharge for watershed WE38 (years 1990-1995). Regression line with 95% confidence intervals follows the basic power equation $C=aQ^b$ with values: a=11.97 and b=0.113.

Nonmonotonic forms add complexity to the method and are not pursued in the present study. Statistically significant correlations can be screened by computing the rank correlation coefficient (RCC) and selecting a threshold significance probability. The RCC is not dependent upon an underlying regression-equation form. It is sometimes appropriate for data to be fitted continuously in a piecewise manner over different ranges of Q with different equations. An example is the piecewise, simultaneously constrained curve fitting in Bonta (2000) for a sediment rating curve using equation 2 (simple power relationship) for two ranges of Q. The piecewise-linear approach is also used in the last section of this report (Case Study) using NO_3-N data.

Concentration and Load Rate Duration Curves (CDCs and LDCs)

There are three basic forms of concentration duration curves (as noted above, refer to Figure 4) – those developed from C-Q correlation regressions that have a positive slope, those having a negative slope, or those that are statistically independent (i.e., no relationship). The following discussion will be based on the simple power equation ($C = a\,Q^b$; Eqn. 2) where the slope, and therefore the exponent (b), is greater than 0. This relationship is illustrated in Figure 5, for SO_4^{2-} (sulfate) concentration data from watershed WE38, for the years 1990 to 1995. The regression line is significant ($p<0.001$, $r^2=0.51$), yielding values for a and b equal to 11.97 and 0.113, respectively. Confidence limits are computed at the 95 percent level. CDCs and LDCs may be constructed in two ways, using the SO_4^{2-} data. The empirical concentration and load data (i.e., raw data) can be sorted according to flow ranking to yield a rough CDC or LDC, as shown in Figure 6 and Figure 7. Also shown, the regression equation can be used to calculate both the CDC and LDC, providing 95% confidence intervals. For calculating load rates (LR) from Eqn. 2, the flow (Q) is first converted to units of liters per second (L/sec) and the following equation is used:

$$LR\ (\text{kg/sec}) = CQ*10^{-6} = aQ^bQ*10^{-6} = aQ^{(1+b)}*10^{-6} \qquad (5)$$

where C is concentration in mg/L, and 10^{-6} converts mg to kg. The reader is referred to Bonta and Cleland (2003) for a more complete treatment.

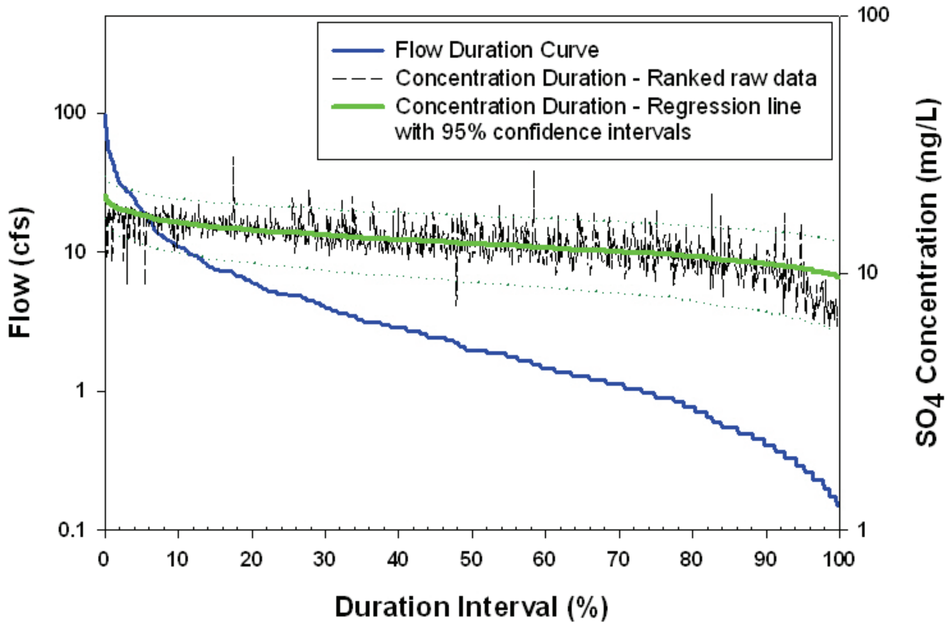

Figure 6. Flow and concentration duration curves (FDC and CDCs) for SO_4^{2-} concentration data for watershed WE38, years 1990-1995. CDCs are shown for raw data and regression equation based on the positive correlation between SO_4^{2-} and flow.

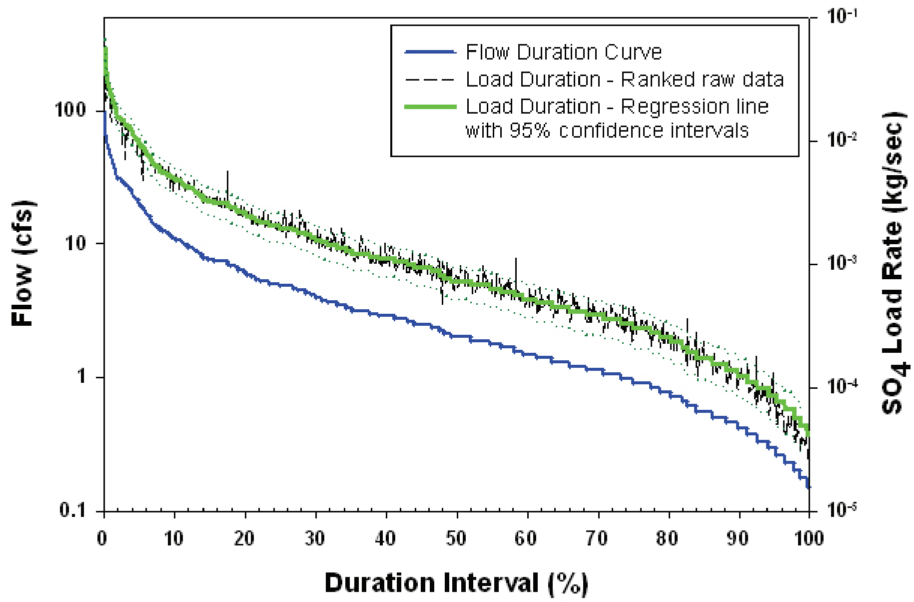

Figure 7. Flow and load duration curves (FDC and LDCs) for SO_4^{2-} concentration data for watershed WE38, years 1990-1995. LDCs are shown for raw data and regression equation based on the positive correlation between SO_4^{2-} and flow.

Assumptions and Limitations

Using DCs with regression relationships requires several assumptions regarding data, analysis, and physical conditions. Extrapolation of data beyond observed data limits, using the form of the C-Q equation chosen, is assumed to be valid. Assuming validity beyond observed data is critical because most data sets consist of a limited number of observations, and very few (if any) contain the maximum and minimum values for a given population (e.g., all flow conditions for a given watershed). All of the basic assumptions underlying regression analysis must be met. The FDC is assumed to be stable so that errors due to FDC characterization of watershed flows are minimized. However, an analysis of error in FDCs can be made with uncertainty analysis and the derived distribution method as outlined in Bonta and Cleland (2003). The underlying flow and concentration data need to be of high quality. The watershed is assumed to be stable, and there should be no factors that would change C-Q relations (e.g., anthropogenic factors, etc.). Best management practices implementation is allowed, but the initiation of BMPs begins a new set of data with which to compare baseline conditions. Furthermore, the C-Q relationships are assumed to be stable for all precipitation events (i.e., non-uniform precipitation and runoff over a basin does not significantly alter C-Q relationship).

Concepts for Using Duration Curves to Quantify Changes in Watershed Condition

Duration curves can be used to quantify changes in flows, load rates, and concentrations over time due to the implementation of management practices (BMPs). This quantification can apply at specific discharges or over intervals of flow that might be important. For example, Figure 8A diagrammatically shows a concentration reduction value of CR mg/L after BMP implementation compared with the baseline data for the 1 percent exceedance (points A to B). Similarly, Figure 8B shows a load-rate reduction (LRR) in kg/day (points C to D). The *exceedance reduction* (ER; equals risk reduction) can also be obtained from Figure 8. For example, starting at point C in Figure 8B (1 percent), the risk for the same baseline daily load rate is at point E after BMP implementation (0.02 percent, a difference of 0.98 percent, which happens to be a 98 percent reduction in exceedance). Although Figure 8 is a simplification of quantifying the impact of a BMP, it illustrates the potential for using duration curves for tracking changes in watershed response after BMP implementation. A reduction in concentration or load rate can be obtained by a reduction in flow rates and/or a change in the C-Q relation. For example, Bonta (2003) documents how C-Q regression parameters change due to changing land disturbances caused by geology and mining and reclamation activities. The DC approach to quantifying stream water changes can be used in planning by estimating a change in regression line parameters, and constructing CDCs and LDCs. However, parameter estimation for changing land uses is beyond the scope of the present study. Using DCs for BMP evaluation is useful beyond evaluating measured data, as they can be used to evaluate watershed model outputs as well. A case study using the CR and LRR approach for quantifying changes in watershed water quality is presented in the last section of this report.

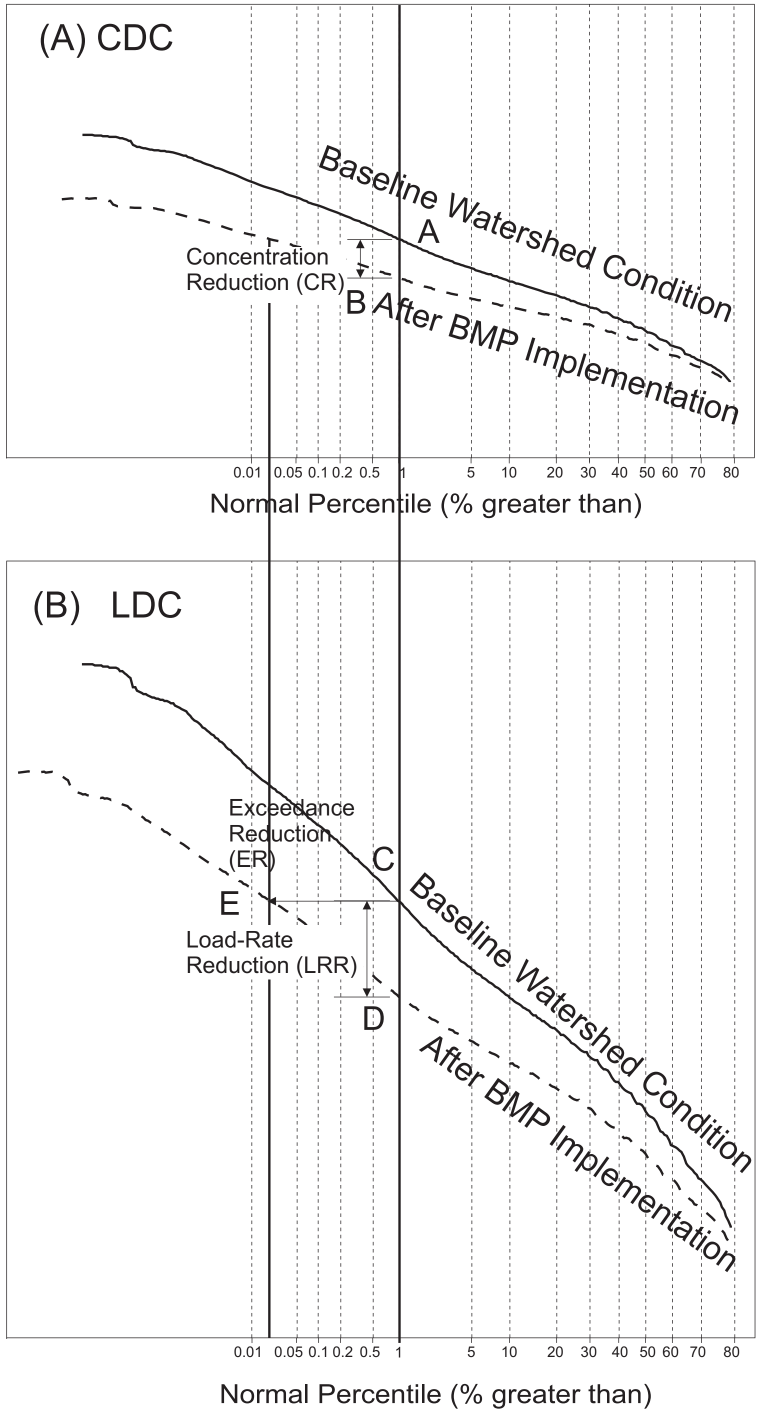

Figure 8. Conceptual depiction of using duration curves to quantify changes in water quality following implementation of management practices. (A) Concentration duration curves show concentration reduction; and (B) Load-rate duration curves show reductions in pollutant loading (Bonta and Cleland, 2003).

Minimum Number of Stream-Flow Samples Necessary for the Construction of Duration Curves

Introduction

While DCs can supplement watershed analysis, their limitations and utility must be explored to provide guidance on their use. In particular, the minimum number of water samples that must be collected to provide reliable CDCs and LDCs is unknown. This is important for new data-collection programs and also when using historic data sets. The high cost of field collection of water samples and laboratory water quality analyses requires guidance on the minimum number of stream samples necessary to obtain a desired level of confidence in a given analysis of condition. Obtaining more samples than necessary can be costly, and the value of additional data is questionable. This is especially important in developing watersheds and BMP implementation studies because the duration of pretreatment conditions is often short, due to budget, time, and physical watershed constraints. Having guidance on the minimum number of samples necessary to obtain reliable water quality and quantity condition assessments allows practitioners to allocate human and fiscal resources more efficiently. The question can only be answered by exploring data sets for which there is a long stream-discharge record and corresponding set of water quality samples. The question addressed in this section concerns whether the minimum number of samples should be based on C-Q regression stability or on the convergence of DCs to an underlying watershed characteristic. An exploratory study was conducted into these two approaches to determine the minimum number of water samples required for characterization of concentration (C) - flow rate (Q) regressions using a power equation, and use of CDCs and LDCs.

Data

Constituent SO_4 from WE38 is used in the present study, for which there are 2290 water samples. Sulfate data exhibited a positive correlation with flow rate, yielding values for a = 8.32 and b = 0.109 for the regression (Figure 9).

Approach to Regression Equations for WE38

The approach to evaluating the minimum number of samples was to use Monte Carlo simulation from subsets of the data. Subsets of water quality samples were obtained by randomly sampling, without replacement, from all available SO_4 data. Target sample sizes of 5, 10, 15, 20, 30, 50, 75, 100, 200, 300, 500, 1000, 1600, 2000, and 2200 observations were obtained. Fifty replicates of a target sample size were generated for a total of 700 subsets. Resulting regressions are referred to as “random regressions”. The estimates of parameters a and b from Eqn. 2 are compared with the corresponding regression parameters estimated from the entire baseline data set. A regression was considered statistically significant if the significance probability was less than or equal to 0.10.

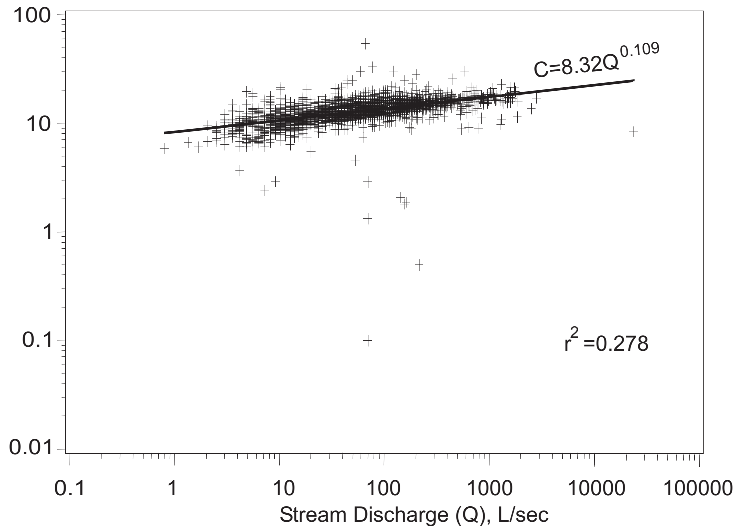

Figure 9. Concentration (C) - discharge (Q) relationships at WE38 for SO_4.

Baseline CDCs and LDCs were developed using parameters in Eqn. 2, with the "instantaneous" FDC providing the flow data used in regressions. The baseline CDCs and LDCs were the benchmarks against which all CDCs and LDCs were compared. The difference in concentration, CDC (random regression) minus CDC (baseline), was computed at each flow and the mean difference in concentration computed. Differences and means for LDCs were similarly computed. The mean differences were examined to estimate a minimum sample size. If a random regression for SO_4 had a negative slope (*b*), the normal percentile for the CDC was not corrected even though the slope for the baseline CDC is positive, thus illustrating the potential for error associated with small samples sizes.

Effects of Sample Size Based on Regression Analysis

Visually, plots of regression parameter variation are characterized by three regions (Figure 10a): 1) *wide* variability for smaller samples tending toward narrow variability as sample size increases; 2) narrow but constant variability for larger sample sizes; and 3) smaller but approximately constant variability for the largest sample sizes. After about 25 samples (parameter *b*) to 35 samples (parameter *a*) for SO_4, both *a* and *b* stabilize to a constant narrow variation up to about 400 samples for *a* and about 150 samples for *b* (Figure 10a and b). Coefficients in this range of sample sizes are within +/- 0.2 units (2% to 3%) of that found using all data (Figure 10a). Most exponents are within +/- 0.02 units (16% to 17%) of that found using all data (Figure 10b). Sample sizes greater than about 400 samples (*a*, Figure 10a) and about 150 samples for *b* (Figure 10b) result in little variation in regression parameters.

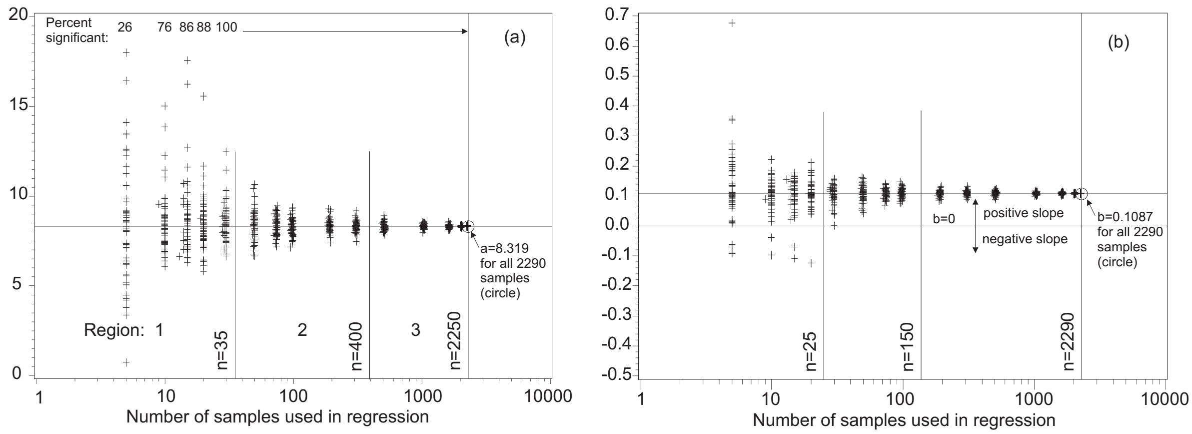

Figure 10. Variation in regression parameters (Eqn. 1) with sample size in random regressions for SO_4: a) coefficient a; b) exponent b.

Not all regressions were statistically significant for sample sizes less than 30 (Figure 10a). For a sample size of 5, only 26% of regressions were statistically significant for SO_4. For a sample size of 10, 76% of regressions were significant. These percentages increased rapidly with increasing sample size to 30 samples after which 100% of all regressions were significant. The baseline slope parameter (*b*) for SO_4 was positive, however, the random regressions showed that slope can vary between negative and positive values for both constituents for sample sizes of 30 or less (Figure 10b).

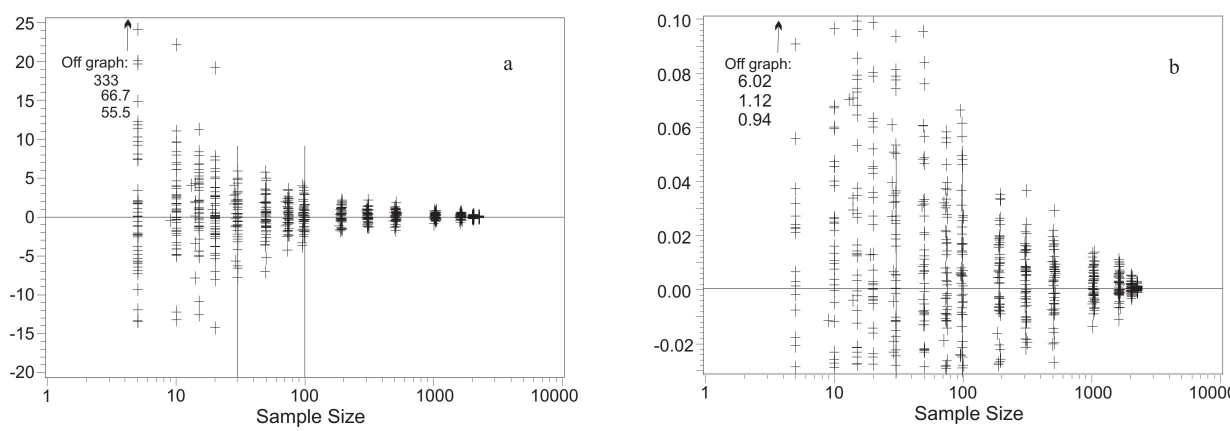

Figure 11. Variation in mean difference between duration curves developed from random regressions and baseline duration curves, with sample size in random regressions for SO_4: a) CDC; b) LDC.

Effects of Sample Size on CDCs and LDCs

Mean differences are quantified in Figure 11 between the baseline CDC (and LDC) computed from the regression developed using all C-Q data and CDCs (and LDCs) computed using random regressions developed with smaller sample sizes. For sample sizes less than about 30, the range of mean differences decreased rapidly with increasing sample size. For n=5, large mean differences plotted off the graphs in Figure 11. SO_4

mean-difference plots for CDCs and LDCs (Figure 11a and 11b, respectively) show that for sample sizes between 30 and 100 that mean differences do not vary much. After about 100 samples, there is little variability in mean differences for SO_4. LDC differences are of the order of only ± 0.01 to 0.03 (greater than 30 samples; Figure 11b).

The variability in mean differences for CDCs and LDCs for SO_4 are selectively illustrated in Figure 12 and Figure 13, respectively. CDCs for sample sizes less than 30 for SO_4 all showed some positively sloped CDCs because of individual random regressions with a negative exponent in Eqn. 1 (e.g., Figure 12a for n=5). Negative exponents are apparent in smaller sample sizes in Figure 12b. CDCs with regression sample sizes larger than 100 quickly approach the baseline CDC (Figure 12d). The trend toward reducing CDC variability about the baseline CDC is apparent in Figure 12a through d as sample size increases. For LDCs, the small mean differences in Figure 13 are illustrated by the small variability in LDCs about the baseline LDC. LDCs corresponding to CDCs in Figure 13, show much less visual variability than apparent in Figure 12 for concentrations.

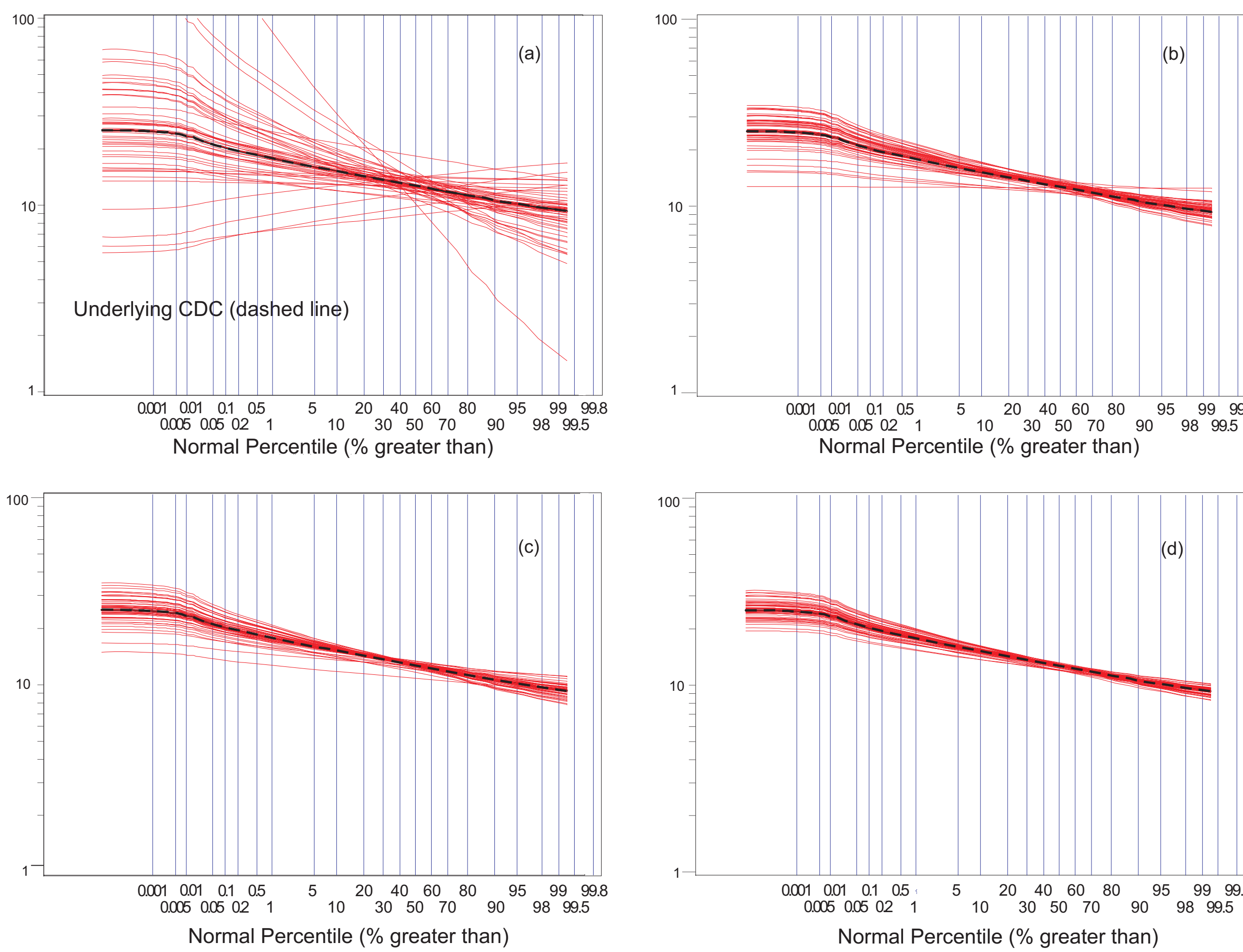

Figure 12. Normal probability plots of CDC for SO_4 for sample sizes of: a) n=5; b) n=30; c) n=50; d) n=100.

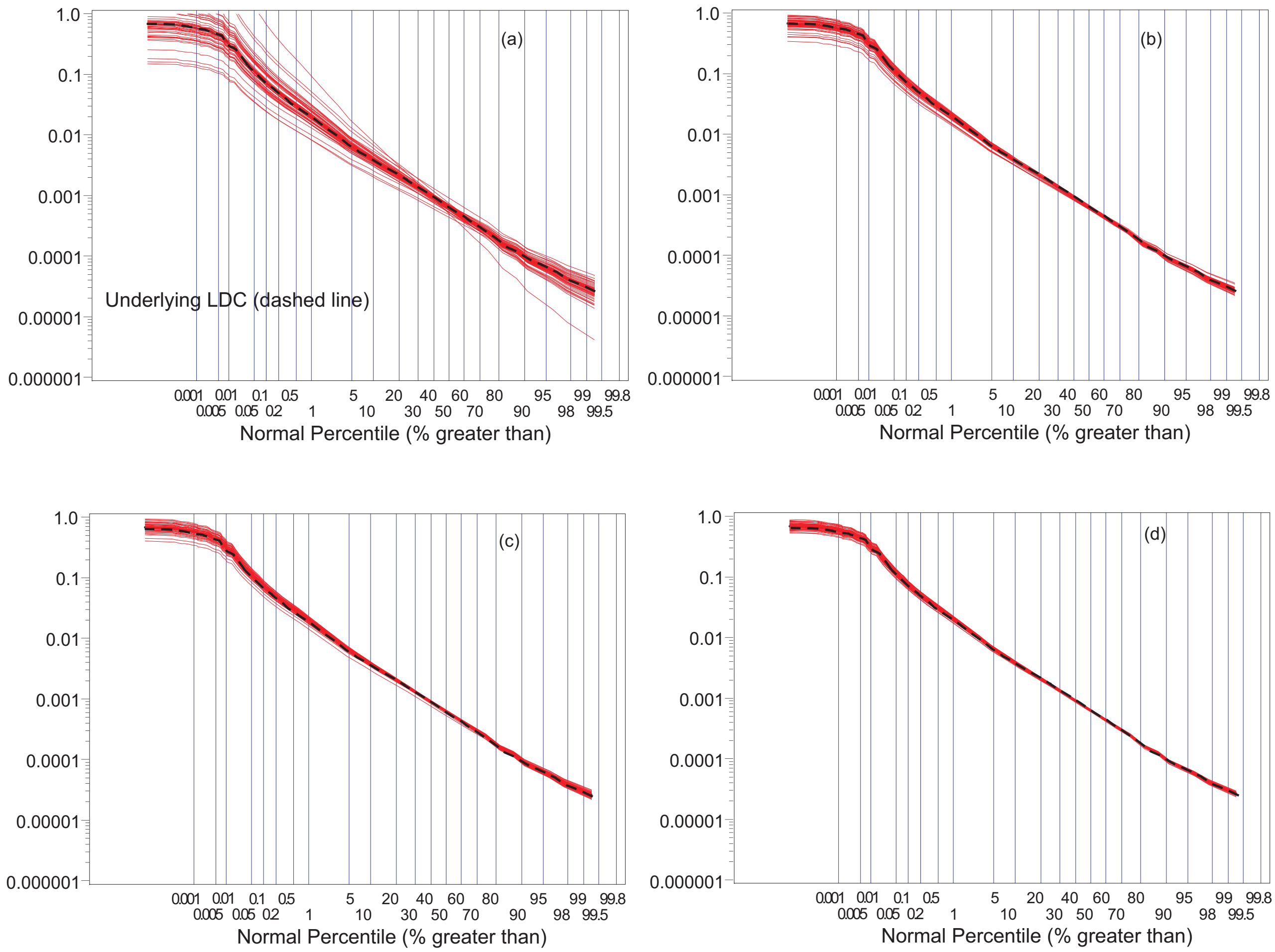

Figure 13. Normal probability plots of LDCs for SO_4 for sample sizes of: a) n=5; b) n=30; c) n=50; d) n=100.

Summary and Conclusions Regarding Data Set Sample Size

Three regions were found in plots of regression parameters and differences between duration curves versus sample size variability. The boundaries of the regions were different for the two approaches. The three regions resulted in recommendations for minimum and maximum sample sizes. The regression-FDC and duration-curve approaches to determining minimum sample sizes result in similar minimum sample size recommendations. However, they differ in the number of samples, beyond which there is no noticeable improvement in variability in parameter estimates or differences between baseline and randomly developed CDCs and LDCs.

The results suggest that a sample size of no less than about 35 samples is needed to minimally characterize the C-Q data for SO_4 for watershed WE38 to avoid improper regression slopes and non-statistically significant regressions. Beyond 35 samples, variation in parameters is roughly constant with slow convergence toward baseline values. The different sample sizes at this point could be related to constituent behavior in the watershed, magnitudes of the parameters, snowmelt effects, effects of season of year, hydrograph position of the samples, and possible mischaracterization of the C-Q relationship by equation 2. Separating the data according to position of the samples on the hydrograph (i.e., rising/falling limbs, etc.) and by growing and dormant seasons may reduce the variability observed in Figure 10 (see Case Study section for evaluation by season). Smaller minimum required sample sizes might result because of the smaller expected variability. Based on the data evaluated by regression analysis in the present study, 50 samples is the minimum sample size suggested. After about 150 to 400 samples, the variability in parameter estimates decreases to a low value, and the value of additional data is questionable.

The exploratory study in this section into the minimum of number of water samples required for adequate characterization of concentration (C) - flow rate (Q) regressions and subsequent development of concentration and load-rate duration curves (CDCs and LDCs) led to the following conclusions:

- A minimum of about 25-35 samples is required to reach an acceptable level of coefficient and exponent variability for SO_4. Narrow parameter variability results with sample numbers larger than about 150-400 samples for SO_4.
- Differences between CDCs and LDCs suggest that 30 samples are adequate for SO_4 with no noticeable improvement in trends of the duration curves after about 100 samples.
- The regression and duration-curve approaches result in similar recommendations for minimum sample sizes, but the duration curve approach suggests a lesser maximum number of samples, beyond which there is no noticeable improvement in differences between baseline and randomly developed CDCs and LDCs compared with the regression approach.
- Based on the combined approaches, 50 samples is the suggested minimum sample size to reduce variability of regression parameters and differences for CDCs and LDCs. There is little benefit derived from obtaining more than about 100 samples, and the value of obtaining additional data is questionable. In the present study, 50 samples represent only about 2% of the total number of samples available for analysis. One hundred samples represent only 4% of the total data set available. The additional 96% to 98% of the C-Q data do not appear to be valuable for general watershed characterization from strictly regression, CDC, or LDC points of view. However, the additional data can be valuable for other objectives such as studies of seasonal variations, sources of chemical constituents, modeling, climate change, nonstationarity, and land-management effects, etc.

Quantifying Uncertainty in the Use of Flow Averaging, and Daily vs. Instantaneous Flows

Introduction to the Temporal Component of Flow Data

Flow duration curves are characterized by the time base of the data used in their development. Given the same watershed flow data, FDCs developed using minute, daily, weekly, etc., time-step data will have different characteristics (Searcy, 1959). Serial flow data, sampled at regular intervals, is important because it provides some assurance – especially with larger data sets and longer periods of time – that the full range *and* distribution of flow conditions is represented by the duration curve. The best available source for flow data is the U.S. Geological Survey, which provides online, downloadable access to data sets with both 30 minute and daily time steps (http://waterdata.usgs.gov/nwis/sw). The U.S. Department of Agriculture, Agricultural Research Service (ARS), also provides online access to hydrology and climate data (http://hydrolab.arsusda.gov/wdc/arswater.html). Duration curves can be constructed by using monthly or opportunistic sampling approaches, but the results need to be interpreted cautiously because the limited data set may not accurately represent the full range of flow conditions or their incidence of occurrence.

In the routine development of duration curves, water-resource managers need to be able to judge whether they can use commonly available average daily flow data to develop FDCs, even when water-quality samples are obtained instantaneously. Samples of runoff are often taken instantaneously by automatic samplers or manually, and do not represent the chemistry for average daily flow rates. Instantaneous flow data, measured at the time water quality samples are taken, provides a more accurate FDC and resultant CDC or LDC. Errors are more likely to occur for high flow conditions in smaller, flashier watersheds where peak discharge occurs quickly and recedes on an hourly time scale, as depicted in Figure 2. Figure 2 shows that the average daily flow rate for WS174 at Coshocton, Ohio, of 63.8 L/s was only 5 percent of the instantaneous peak flow rate (1,238 L/s) for the day. For data from WS174, streamflow is recorded in breakpoint format. This data recording format captures the most detail, but for some applications data of equal time intervals is all that is available (e.g., WE38). Mean daily discharge is likely to be least accurate at representing high flows but should be adequate for representing the flow regime under non-flood conditions. A separate question, addressed in detail in the following section, is whether the FDCs based on averaged flows can be substituted for FDCs based on instantaneous flows as the independent variable in regressions to develop CDCs and LDCs without compromising their accuracy for all flow conditions.

Method for Data Averaging

The effects of averaging period used to compute FDCs on subsequent CDCs and LDCs are examined by using the regression equations (Eqns. 2 and 5) developed from all data for SO_4 (instantaneous flow rate at time of stream-water sampling) with averaged flow rates calculated using different periods of time. The baseline CDC and LDC computed using all C-Q data with the instantaneous FDC is used as the benchmark. An average flow rate is computed by dividing the accumulated flow volume during the averaging time periods by the length of the time period. FDCs were developed using average flow rates over averaging periods of 5 min, 10 min, 15 min, 20 min, 30 min, 1 hr, 2 hr, 4 hr, 6 hr, 12 hr, and 24 hr. These average flow rates are used to develop CDCs and LDCs from equations 2 and 5, and to explore trends of the results with averaging time. The mean of the ratios of the individual CDC and LDC values to the baseline CDC and LDC at selected flow points is plotted against flow averaging time to quantify the effects of using averaged FDCs. Maximum flows are examined separately. Average time-weighted concentrations and load rates using the weights from the duration curves for each averaging time are compared with instantaneous values, and selected FDCs, CDCs, and LDCs are plotted.

Effects of Averaging Time on CDCs and LDCs

Average time-weighted concentrations and load rates computed from the duration curves for SO_4 are practically the same for all averaging times compared with the instantaneous duration curves (Table 1) as seen by the ratios near unity. Mean weighted concentration ratios range from only 1.000 to 1.003 of instantaneous averages and load rates range from 0.969 to 1.000. The small differences in averages are in part due to the small exponents in Eqn. 2. Plots for the two most extreme cases (instantaneous and average daily flows) show the curves lie almost entirely on top of one another (Figure 14; SO_4 only). The curves tend to diverge slightly at larger flow rates where maximum averaged flows are not representative of instantaneous flows as discussed next.

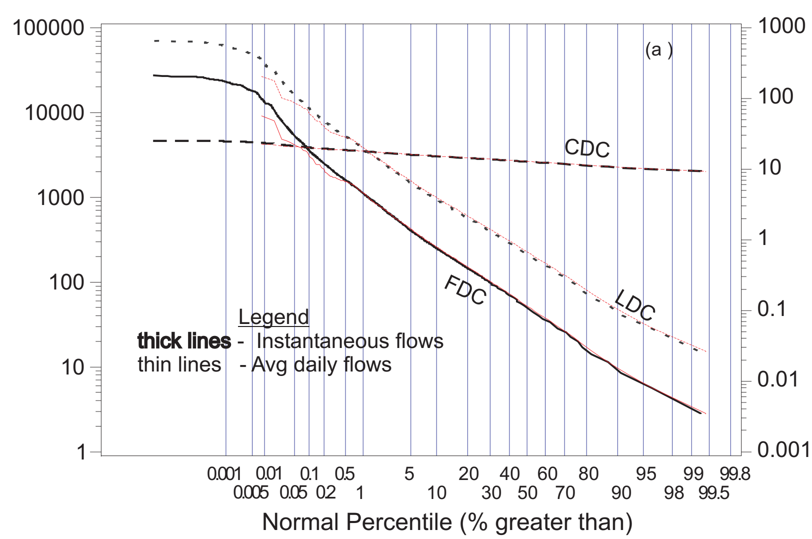

Figure 14. FDC, CDC, and LDC for SO_4 data from watershed WE38, computed using instantaneous flow (black lines) and average daily flows (red lines).

While there is little effect of averaged flow rates on the overall structure of CDCs and LDCs in Figure 14, the largest flows computed for the averaged FDCs are reduced because of the averaging. This can be seen in Table 2 where the maximum flow for the instantaneous (raw) data is 27533 L/sec, whereas the maximum average daily flow is 18201 L/sec, 66% of the maximum recorded flow. This does not have a noticeable impact on SO_4 concentrations where it can be seen that SO_4 concentration for daily flows is 96% of that associated with instantaneous flow (Table 2). The small differences are due to small exponents (Eqn. 2). The maximum load rates, however, are significantly affected. For example, maximum load rates computed with average daily flows are only 63% (SO_4) of that of the maximum instantaneous flow.

FDCs developed from different flow-averaging times (when used as the independent variable in Eqns. 2 and 5 to develop CDCs and LDCs) do not appear to affect CDCs and LDCs using the SO_4 data from Watershed WE38. This suggests that using commonly-available average daily flows for water quality analyses may allow a reasonable characterization of chemical concentrations for watersheds of 7.3 km^2 and larger. However, as shown in Figure 2 for a gauged 21.4-ha watershed at the NAEW in Coshocton, Ohio, average daily flow was only 5% of the measured peak runoff for one large monitored runoff event. In the present study, peak average daily flow was 66% of measured instantaneous flow rate. The flashy character of runoff from “smaller watersheds” may preclude the substitution of average daily flows for measured instantaneous flow rates. However, guidance on watershed size limitations, and the behavior of water quality constituents that behave differently in response to flow rate, requires further study.

Recommendations Based on the Effects of Averaging Time

One advantage of the duration-curve approach to evaluating water quality data is that it has the potential to convert concentration data collected in the field to load rate data required by regulatory agencies, such as for TMDLs (mass/day; Bonta and Cleland, 2003). The nearly identical load rates found for all averaging times (that include average daily flows) suggests that the conversion is facilitated by assuming that water samples collected instantaneously can be used with average daily flows to yield a mass/day (TMDL). Average daily flows are a common form of flow data available to a practitioner. A further advantage is that the mass/day value also has a percent time of exceedance associated with it. While there was near equivalence of CDCs and LDCs developed from instantaneous and average daily flows in the present study, other parameters with larger parameter values may show larger differences requiring further study.

Time-weighted averages for the entire range of flows were used in the present study, but it may be desirable for a practitioner to censor the duration curve for specific purposes as suggested by Bonta and Cleland (2003). Selecting flow or percentile ranges in this way may yield different results. This is particularly true if the focus is on larger flow rates. It is not likely that a BMP will be effective for the entire range of flows that can occur (e.g., extreme flooding), and the larger flow rates may be excluded in analyses using the duration curve approach if chemical loads and concentrations cannot be controlled by the BMP. The larger flows and load rates occur infrequently and provide little weight in time-weighted averages. However, the results of the present study suggest that midrange and small instantaneous flow rates may be represented by average daily flows. The practitioner should be aware that maximum concentrations can occur at the smallest flow rates if the exponent in Eqn. 2 is negative. However, the load rates will be larger at the larger flows within the constraints of Eqn. 5. Recognizing this can affect a decision on potential BMPs that are feasible. The use of average daily flows to characterize very small watersheds could introduce significant error depending on constituents and regression-parameter magnitudes. Errors are more pronounced at larger or smaller flows depending on the sign of the exponent in Eqn. 2. A positive correlation results in larger concentration errors for larger flows, and a negative correlation results in larger errors for smaller flows. For larger exponents, the differences will be larger.

Other constituents associated with different erosion and transport mechanisms may reveal limitations on using average daily flows. A simple power relationship (Eqn. 2) was assumed in the present study to characterize the C-Q relationship. Other constituents in the WE38 data show piecewise monotonic and non-monotonic behavior which requires special treatment using the duration curve method. These more complicated representations will likely affect both guidance on minimum required samples sizes and the errors resulting from using average daily flows. An example of a piecewise analysis is shown in the Case Study section of this report.

Table 1. Average constituent concentrations and load rates for the data set computed using a range of flow averaging times.

	Concentration		Load Rate	
Averaging Time	Average SO_4, mg/L	Ratio to instantaneous (SO_4)	Average SO_4, kg/sec	Ratio to instantaneous (SO_4)
instantaneous	12.860	1.00000	0.001896	1.00000
5 min	12.860	1.00001	0.001896	0.99981
10 min	12.860	1.00000	0.001896	0.99975
15 min	12.861	1.00001	0.001895	0.99969
20 min	12.861	1.00002	0.001895	0.99964
30 min	12.861	1.00003	0.001895	0.99939
60 min	12.862	1.00009	0.001894	0.99871
2 hr	12.863	1.00023	0.001891	0.99723
4 hr	12.868	1.00055	0.001886	0.99467
6 hr	12.871	1.00084	0.001881	0.99205
12 hr	12.881	1.00158	0.001865	0.98384
24 hr	12.902	1.00322	0.001838	0.96925

Table 2. Effect of flow averaging times on the maximum flow rate, and on concentration and load rates

Averaging Time	Flow Rates: Max. Flow, L/sec	Flow Rates: Ratio to instantaneous	Concentrations: Max. SO_4, mg/L	Concentrations: Ratio to instantaneous (SO_4)	Load Rates: Max. SO_4, kg/sec	Load Rates: Ratio to instantaneous (SO_4)
instantaneous	27,533	1.00	25.3	1.000	0.696	1.000
5 min	27,082	0.98	25.2	0.998	0.683	0.982
10 min	26,666	0.97	25.2	0.997	0.672	0.965
15 min	26,522	0.96	25.2	0.996	0.668	0.959
20 min	26,301	0.96	25.2	0.995	0.662	0.951
30 min	26,134	0.95	25.1	0.994	0.657	0.944
60 min	25,525	0.93	25.1	0.992	0.640	0.919
2 hr	24,477	0.89	25.0	0.987	0.611	0.878
4 hr	22,486	0.82	24.7	0.978	0.556	0.799
6 hr	20,940	0.76	24.5	0.971	0.514	0.738
12 hr	18,912	0.69	24.3	0.960	0.459	0.659
24 hr	18,201	0.66	24.2	0.956	0.440	0.632

Case Study: Evaluating Monthly, Seasonal and Annual Period Changes in Nitrate Concentration

Objective and Approach

The overall objective for this case study is to illustrate how information can be inferred from DCs to supplement water-quality investigations in river basins. This section provides an example of how the concepts described in Figure 8 can be applied to quantify changes in a water quality constituent. The case study utilizes the unique long-term, WE38 data set and will examine seasons and associated instantaneous FDCs, CDCs, and LDCs, changes in hydrology and water quality during different periods, and possibilities for further analyses. The case study is not fully developed in terms of causality, watershed characterization and the use of complimentary and supplementary data sources and analyses that watershed managers would use in a real world application of the duration curve concept.

Scenarios and Periods of Record

Long, continuous runoff records with concurrent discrete samples of water quality are generally not readily available. However, watershed WE38 flow and NO_3-N data have characteristics that enable the utility of duration curves for comparing changes in water quality to be illustrated. These characteristics include monthly and seasonal differences in the C-Q relationship for NO_3-N, and apparent changes in watershed hydrology within the period of record. FDCs, CDCs, and LDCs were compared within three scenarios: monthly DCs for the entire period of record, DCs for seasons identified from stream flow and ancillary hydrological data, and DCs for three periods of apparent change in the WE38 record. The three scenarios are outlined in Table 3 and are described more fully in subsequent sections. Periods were intervals of time selected according to the three scenarios. Individual combinations of scenarios and periods are referred to as a "scenario.period". For example, scenario 7, period 5 is "7.05". A 10 mg/L reference line is used on concentration graphs for NO_3-N because of its significance as a drinking water standard.

FDCs were constructed using the 5-min data to make instantaneous DCs – no flow averaging was performed (e.g., average daily flows). Regressions between concentration and discharge used instantaneous flows at the time the samples were taken.

Seasonal Distribution of Discharge and NO_3-N Data for WE38

Discharge and NO_3-N concentrations have similar monthly trends, except early in the year, when NO_3-N tends to decrease while discharge increases (Figure 15). CDCs and LDCs are able to capture these two trends separately because flow is expressed through the FDC and concentrations are expressed through C-Q regressions. LDCs combine the effects of both hydrology and water-quality processes. The need to consider seasons of the year is apparent from this figure.

Concentration-Flow Rate Regressions (C-Q)

Preliminary plots of C-Q, for NO_3-N data on a log-log grid for the three scenarios suggested that a 2-equation, piecewise regression, using two power equations (Eqn. 2), would fit the data best for developing CDCs and LDCs. However, sometimes a single power equation was satisfactory. The nonlinear, 2-equation fit was constrained to ensure that the two equations would intersect at a flow rate chosen by inspection of the C-Q data during the fitting process (Q_i). The flow-intersection point varied from period to period within a scenario, highlighting its dependence on watershed conditions and NO_3-N availability and transport conditions. Individual regressions are presented in the following sections.

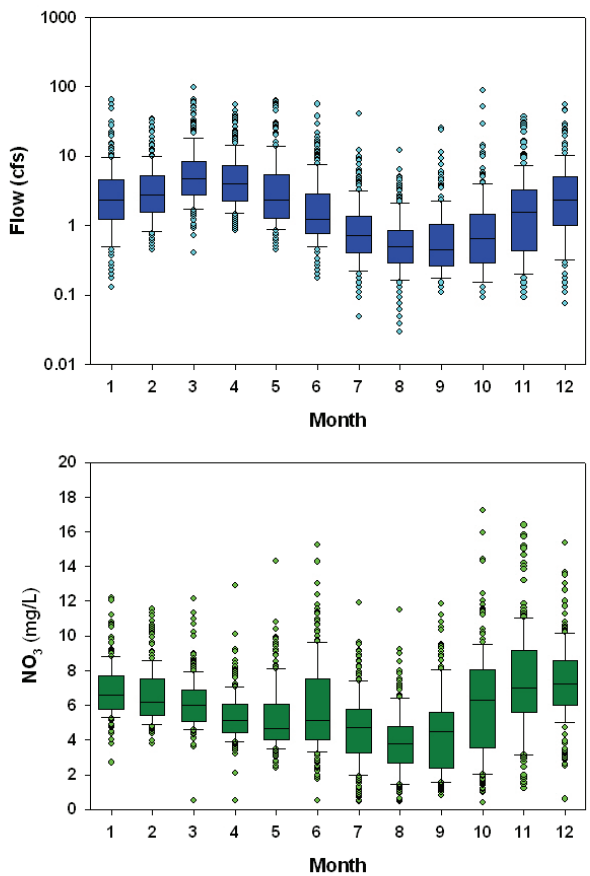

Figure 15. Monthly distribution of flow rate (upper) and NO3-N concentration (lower) for WE38.

Monthly Duration Curves (Scenario 7)

<u>Flow duration curves</u>

Flow data were extracted from the WE38 stream-flow record by whole months (scenario 7, Table 3), and monthly DCs were developed by collapsing all data across years for an individual month to develop a single monthly FDC (Figure 16). Seasonality (by month) is apparent from the FDCs (Figure 16), with August having generally the smallest stream flows and March having the largest. The thinner lines cover the first six months of the year and the thicker lines cover the last six months. The first six months are characterized as having generally larger flows than the second half of the year.

Table 3. Scenarios and periods of data for comparing duration curves.

					Beginning*		Ending*	
Scenario Number	Period Number	Scenario Description	Beginning Date*	Ending Date*	Month	Day	Month	Day
7	1	Monthly DCs	1/1/1984	12/31/2002	1	1	1	31
	2				2	1	2	28
	3				3	1	3	31
	4				4	1	4	30
	5				5	1	5	31
	6				6	1	6	30
	7				7	1	7	31
	8				8	1	8	31
	9				9	1	9	30
	10				10	1	10	31
	11				11	1	11	30
	12				12	1	12	31
8	1	Seasonal DCs	1/1/1984	3/31/2003	4	1	8	31
	2				9	1	11	30
	3				12	1	3	31
9	1	Period DCs	1/1/1984	12/31/1992	0**	0	0	0
	2		1/1/1993	12/31/1998	0	0	0	0
	3		1/1/1999	12/31/2002	0	0	0	0

*Inclusive dates

**A zero month and day implies the entire period of time between beginning and ending dates was used.

It is apparent that the lines tend to graph nearly as straight lines on the log-normal plot, with some concavity, suggesting a possibility for curve fitting using the equation for the normal distribution. The extremes do not tend toward straight lines because insufficient data are available to develop stable FDCs in these regions. The linear tendencies of most of the flows suggest that curve fitting with an extra parameter (z) added to flow rates prior to plotting may straighten the lines (Q+z). This extra parameter, along with the mean and standard deviation suggest possibilities for relating these three parameters with basin characteristics. For example, earlier it was mentioned that the slope of the FDC was a measure of the flashiness of a watershed. The slope of a FDC is the standard deviation and may be related to channel and/or overland-flow steepness or other basin properties. Even the low flow extreme of the FDCs could be related to drainage characteristics (e.g., floodplain soil texture, meandering, geology, etc.). Detailed examination of such relationships is beyond the scope of the present report.

Figure 16 suggests that seasons could be identified from the range of FDCs. For example, the FDCs for the 2-month periods for March-April (7.04-7.05) and July-August (7.07-7.08) (the extreme FDCs), and Nov-Dec (7.11-7.12), could be grouped together to minimize analyses and to allow more water-quality data to be collapsed into the two 2-month periods. This is important because water-quality data are generally scarce and grouping the data for similar hydrological conditions would aid data interpretation.

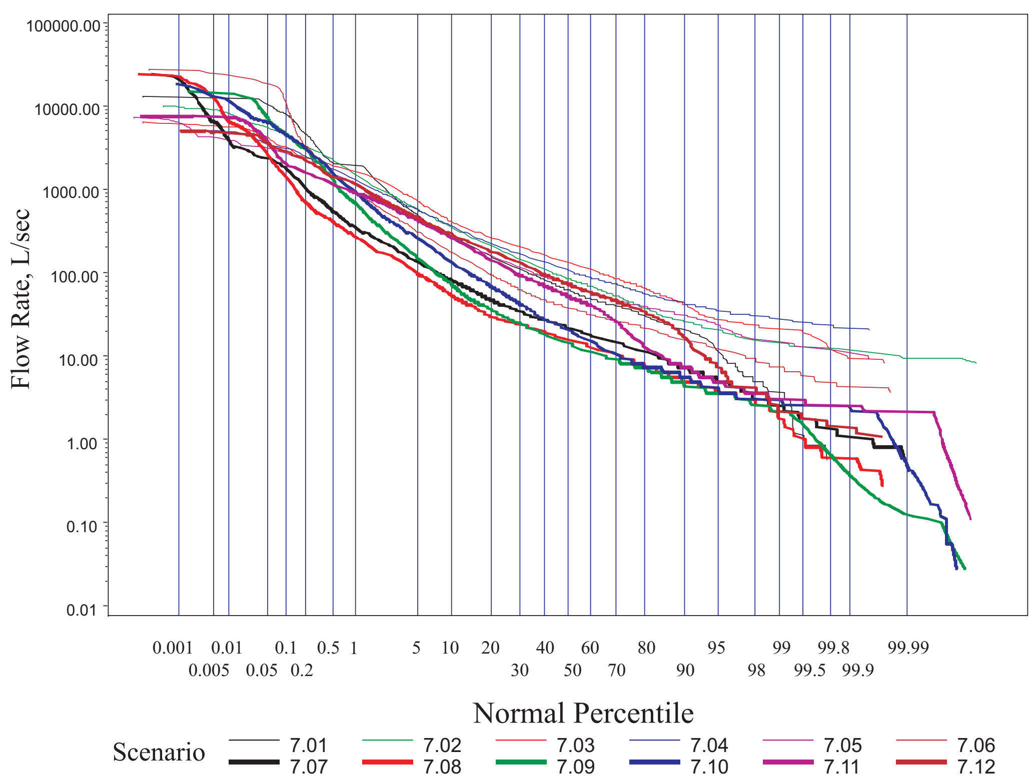

Figure 16. Flow-duration curves for the twelve monthly periods of scenario 7.

<u>Concentration-flow regressions</u>

In addition to the FDCs, plots of concentration vs flow rate (C-Q plots) by month in Figure 17 and Figure 18 show that the relationships between NO_3-N concentrations and discharge vary substantially from one period (month) to the next. The trends in data suggest changing watershed conditions, but causes are unknown for WE38. The results also suggest that collapsing data for periods longer than month-based seasons may add to variability in regressions and that the collapsed period may not contain nonstationary data.

Visually, correlations change from a positive correlation from September through November (Figure 17), to no correlation from December (Figure 17) through March (Figure 18), and then return to a positive correlation with increasing slope from April through August. The need for quantifying the correlations with two simultaneous power equations on some of these monthly plots is apparent by noting the curvilinear trends of the data for a given month. These changes occur in addition to the hydrological changes documented in the FDCs in Figure 16. The causes for changing correlations are unknown for WE38 but changes in water-quality processes and anthropogenic activities in the watershed are most likely factors.

Regression results in Table 4 quantify the correlations in Figure 17 and Figure 18. A smaller *a* parameter is apparent from July through October reflecting generally lower flows in the FDCs (Figure 16). However, the *b* parameter is larger during this time reflecting the steeper slopes of the data trends and suggesting more availability of NO_3-N in the watershed. Parameter *b* values are close to zero from January through March, suggesting a lack of correlation. The lack of correlation can be visually seen in Figure 17 and Figure 18. The *d* values are generally small and suggest that there is no correlation for larger flows for most months. July, August, and September are exceptions. The values for parameter *c* are greatest for October through December. The intersection flow, Q_i, shifts to larger flows during much of the second half of the year. The maximum during April is due to uncertainty because of the beginning of a shift to a positive correlation from no correlation in the previous month.

Table 4. Concentration-flow rate regression parameters for 1- and 2-equation piecewise fits using the form of equation 2 for scenario 7.

	Eqn 2 Parameters*				
	Smaller Flows (<Q_i)		Larger Flows (>=Q_i)		
Scenario.Period**	*a*, L/sec	*b*	*c*, L/sec	*d*	Q_i, L/sec
7.01	7.129	-0.016	NA	NA	NA
7.02	6.856	-0.017	NA	NA	NA
7.03	4.154	0.074	NA	NA	NA
7.04	2.507	0.159	4.764	0.033	158.5
7.05	1.819	0.226	NA	NA	NA
7.06	1.777	0.296	NA	NA	NA
7.07	0.383	0.944	2.533	0.198	12.6
7.08	0.655	0.704	2.056	0.253	12.6
7.09	0.833	0.599	4.249	0.127	31.6
7.10	0.853	0.666	6.816	0.021	25.1
7.11	1.622	0.415	6.710	0.052	50.1
7.12	1.223	0.710	7.271	0.006	12.6

*Parameters *a* and *b* are for the lower flows, and *c* and *d* are the equivalent parameters for larger flows.

** “Period” corresponds to month number.

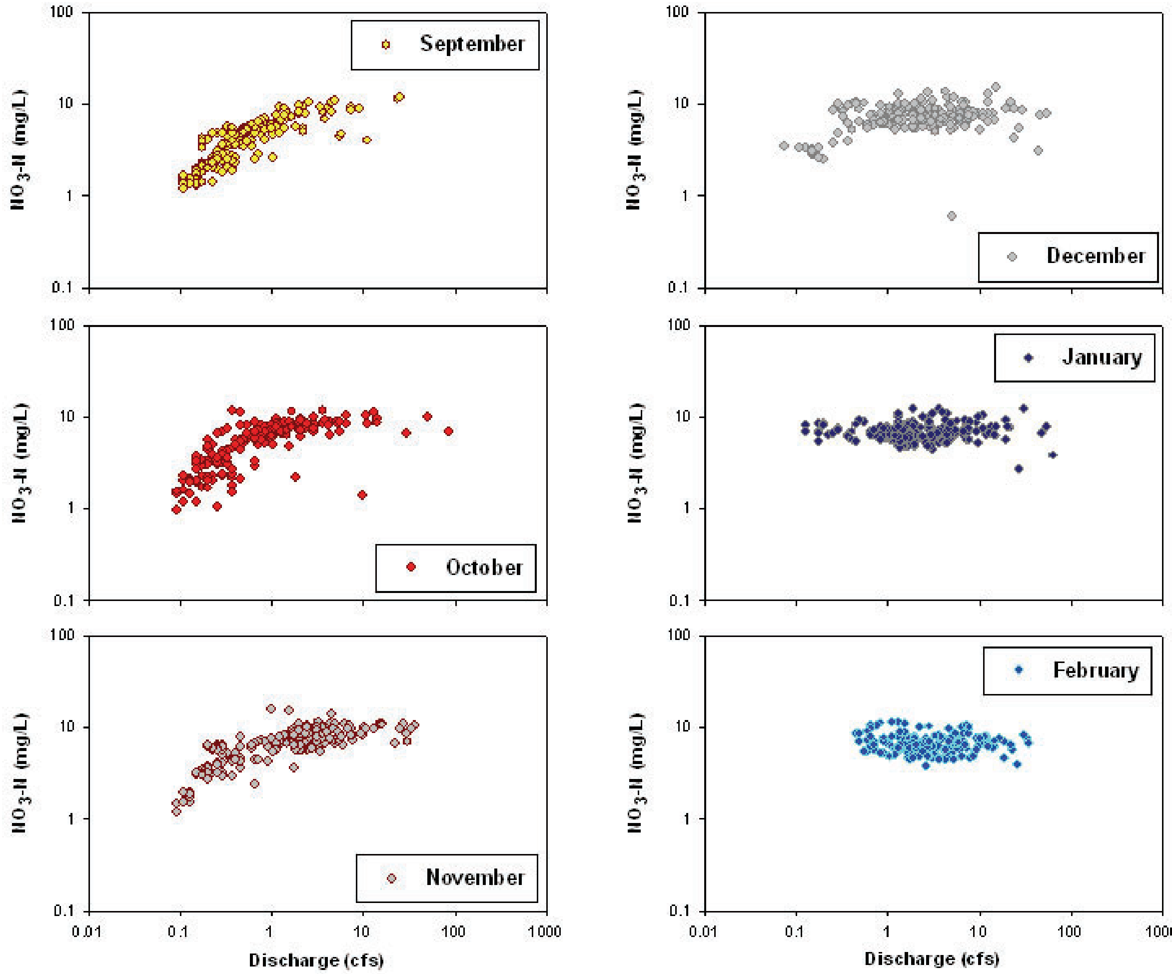

Figure 17. Concentration -flow-rate graphs for NO_3-N for September through February data at WE38.

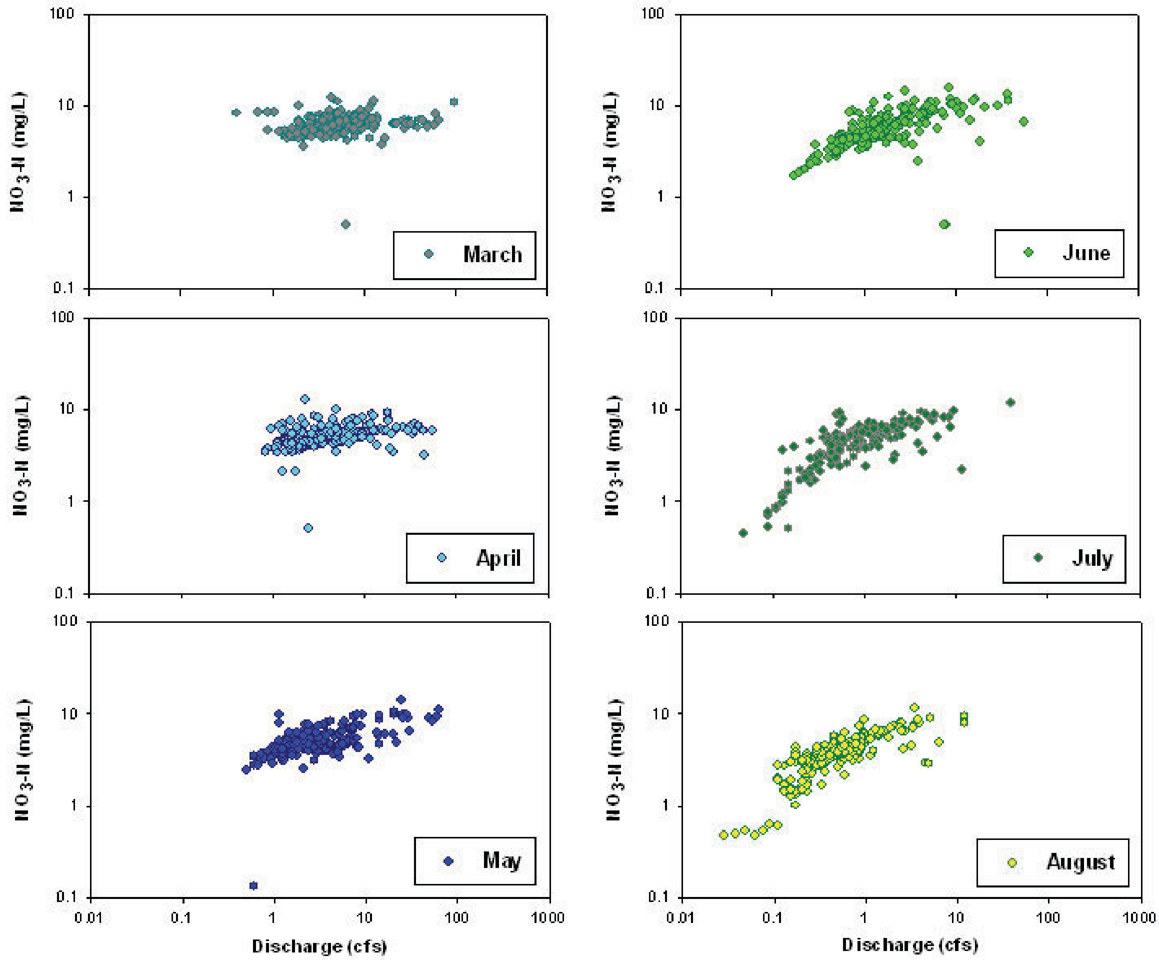

Figure 18. Concentration -flow-rate graphs for NO_3-N for March through August data at WE38.

<u>CDCs for monthly data</u>

Many of the CDCs for the monthly plots (Figure 19) are flat for larger flows, reflecting the weak correlation apparent in Figure 17 and Figure 18 for larger flows (small regression slopes [*b* and *d*] in Table 4). The months of January and February are not plotted due to essentially flat lines for the entire range of concentrations. The intersection points for the regressions are apparent by noting the abrupt change in slopes of the CDCs for the lower concentrations – to the left at larger flows the curves are relatively flat and to the right at smaller flows the curves slope sharply down reflecting the larger low-flow regression slopes (Table 4).

The CDCs show that by considering seasons (months in this scenario), large differences in exceedences are apparent. For example, April concentrations exceed 4 mg/L 99.9% of the time (see 4 mg/L line), while for August and November, 4 mg/L is exceeded 50% of the time. Assuming for discussion that if a standard of 4 mg/L were set for the year, the stream would usually not be in compliance and field sampling conducted in April would almost certainly show noncompliance. The observed level might be due to natural processes that are not controllable, suggesting that seasonal regulated levels might be appropriate. DCs could be used to help establish monthly/seasonal levels. Alternatively, if a land-management improvement practice was implemented in the watershed, any change might be detected sooner using monthly DCs because a subtle monthly change would be masked in the variability of annual data. Both purposes argue for separating flow and concentration data records into seasons.

Another interesting feature in the CDCs of Figure 19 are the lines for May through September above the 10 mg/L drinking-water regulation level, with June reaching nearly 400 mg/L, while the maximum measured NO_3-N concentration at WE38 was 17.2 mg/L. In the case of June, a single equation was found to fit the data best (Table 4), but its regression slope (b=0.296) was greater than the slope parameter of all the months for the larger flows (*d*). The slope value for August was the second largest (d=0.253), and the position of the CDC in Figure 19 was the next largest. Larger and smaller concentrations can be computed using C-Q equations because the equations can be extrapolated, assuming extrapolation is valid, however. Obtaining a field sample at the largest flow rate may not be likely and extrapolated values may be the only way to estimate the concentration at the infrequent flows. This is particularly important in sampling programs of short duration. The use of equations with FDCs makes maximum use of usually small water-quality data sets to provide estimates of concentrations beyond the measured values, an advantage of DCs.

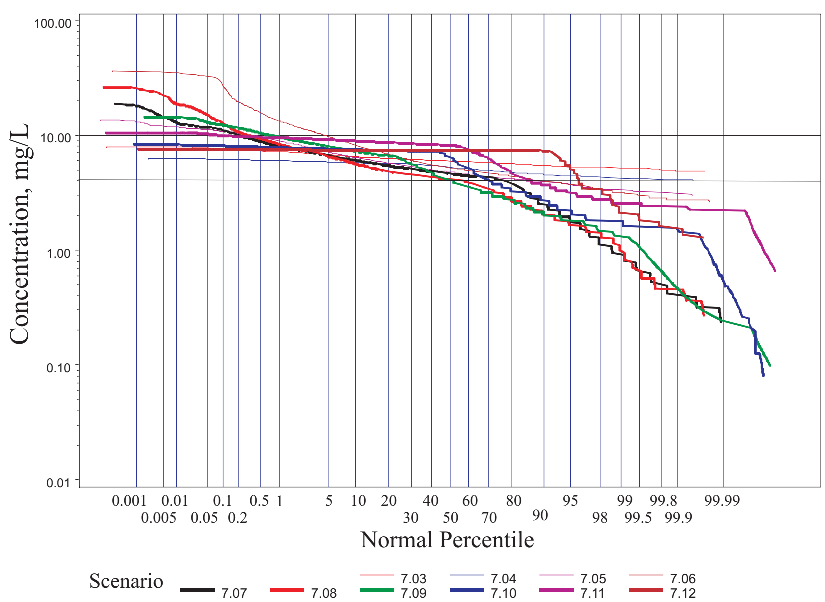

Figure 19. Concentration-duration curves for the 12 periods (months) of scenario 7 for NO_3-N.

LDCs for monthly data

LDCs shown in Figure 20 correspond to the CDCs just presented, and show trends similar to the FDCs with generally larger load rates for the first half of the year. Many of the same statements can be made for LDCs that were made in the previous section for the corresponding CDCs.

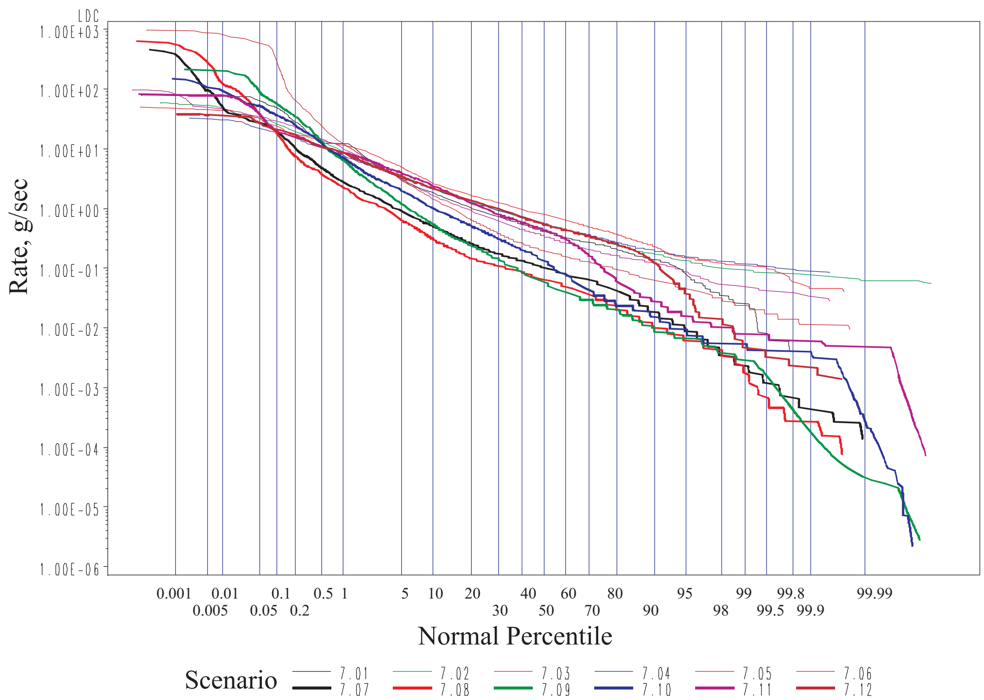

Figure 20. Load-rate-duration curves for the 12 periods (months) of scenario 7 for NO_3-N.

Seasonal Duration Curves (Scenario 8)

The previous section considered characterizing hydrology and water quality strictly on a monthly basis. In this section, seasons are identified using available watershed data, and DCs are developed.

Determining seasons based on hydrology and water quality data for WE38

For WE38, seasons were identified using average monthly water table elevations for seven monitoring wells within WE-38, precipitation, and average monthly flow at the watershed outlet (Bil Gburek (2006) *personal communication*). Average monthly values were normalized by the individual gage's overall annual range. Plots of the normalized values showed that all the wells behaved in a similar pattern that was distinctly different from the stream-discharge plot. Based on the synthesis of all the gages, and changes in slope for the normalized plots, three distinct hydrologic periods were identified: April through August, September through November, and December through March (identified as scenarios 8.01, 8.02, and 8.03, respectively; Figure 21). A notable feature in Figure 21 is the 1-month lag of well levels following stream flow.

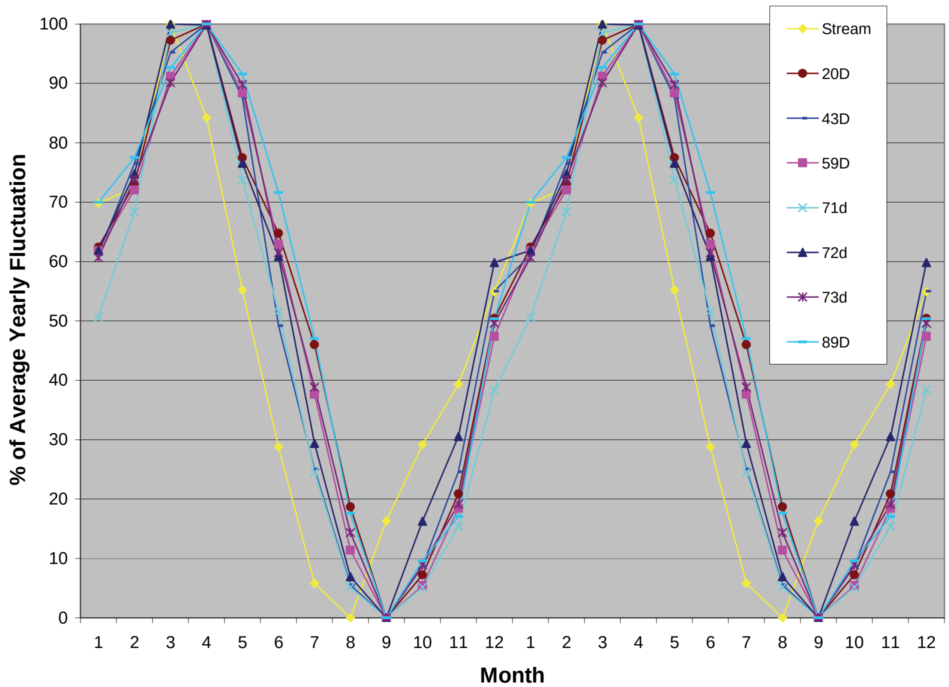

Figure 21. Normalized plots of monitoring well levels and stream flow data for WE38; used to identify seasons for scenario 8 (Bil Gburek (2006) *personal communication*).

<u>FDCs for seasonal data</u>

The data were collapsed across the entire period of record for the months comprising each season, and FDCs developed for the three seasons (Figure 22). Season 3 (Dec-Mar) had the largest flows and season 2 (Sept-Nov) had the smallest flows. As for scenario 7, the visual difference between seasonal discharges is apparent.

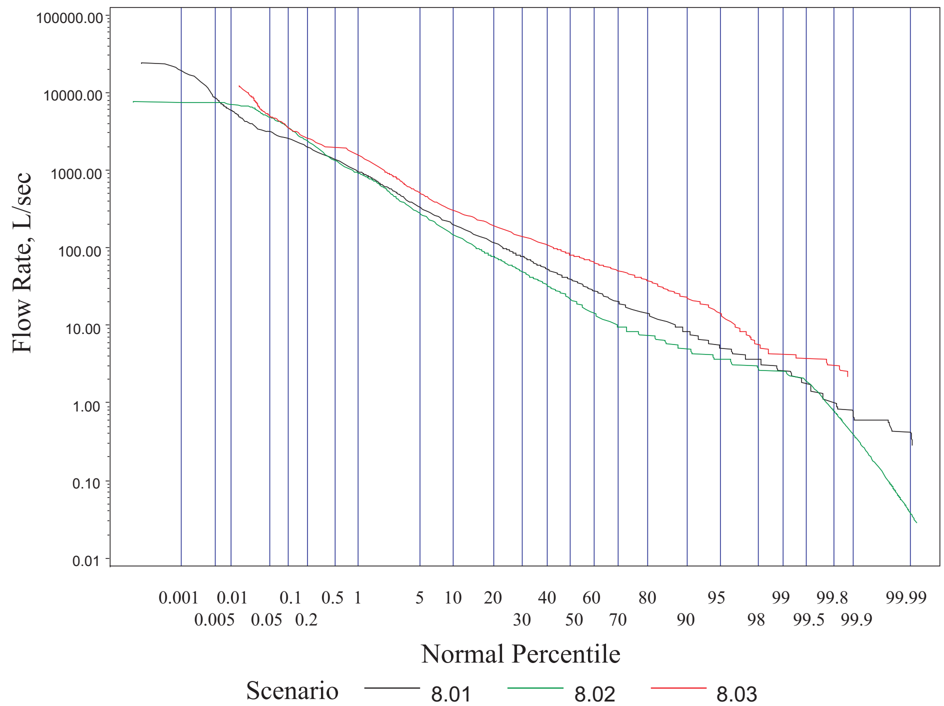

Figure 22. Flow-duration curve for the three periods (seasons) of scenario 8.

C-Q regressions for seasonal data

The seasons identified by examining the variety of hydrological data available for WE38 showed visually different C-Q relationships. The two piecewise regressions for scenario 8.01 and 8.02 in Figure 23 had identical intersection flow values (Q_i=12.6 L/sec; Table 5), while Q_i=39.8 L/sec fit the data better for scenario 8.03. The trend of the points for 8.03 was noticeably flatter for the range of sampled flows. This is consistent with winter data for scenario 7. The concentrations for 8.02 were generally larger than 8.01 for the same flow rates, resulting in larger coefficients (*a* and *c*). The slopes of the corresponding 8.01 and 8.02 piecewise lines were similar for both small and large flows. These parameter combinations resulted in scenarios 8.01 and 8.02 being visually parallel to one another, with 8.02 having higher concentrations.

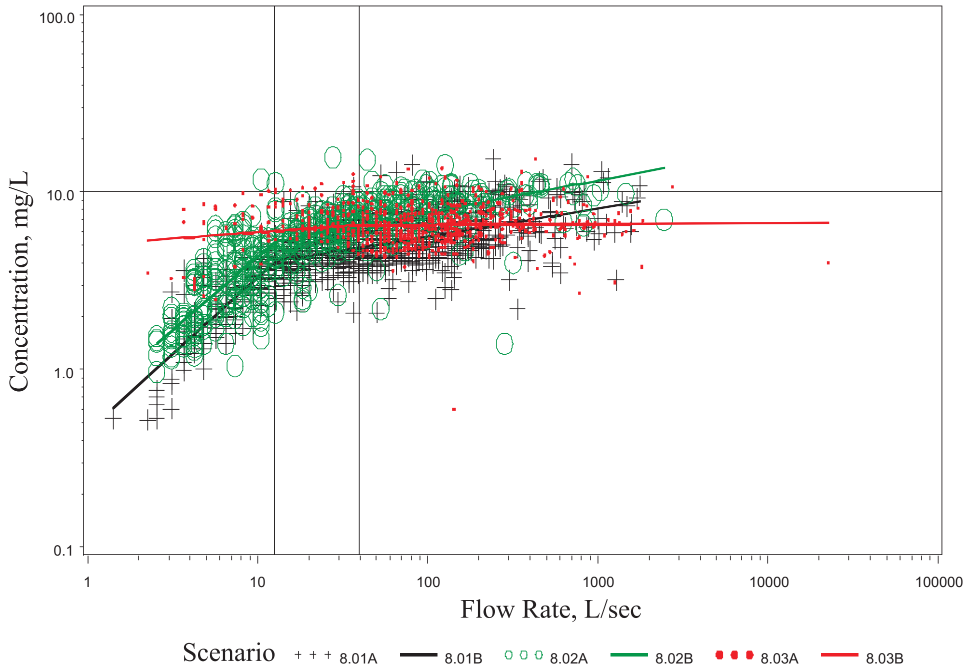

Figure 23. Piecewise-linear concentration-flow rate regressions for scenario 8. A refers to the graph of empirical data and B refers to the regression for each scenario.

Table 5. Concentration-flow rate regression parameters for a 2-equation piecewise fit using the form of equation 2 for scenario 8.

	Eqn 2 Parameters*				
	Smaller Flows (<Q_i)		Larger Flows (>=Q_i)		
Scenario.Period	*a*, L/sec	*b*	*c*, L/sec	*d*	Q_i, L/sec
8.01	0.451	0.868	2.732	0.157	12.6
8.02	0.646	0.827	3.309	0.182	12.6
8.03	5.050	0.070	6.472	0.003	39.8

*Parameters *a* and *b* are for the lower flows, and *c* and *d* are the equivalent parameters for larger flows.

CDCs for seasonal data

The combination of FDCs and C-Q regressions between periods 8.01 and 8.02 made the CDCs similar for lower discharges (Figure 24). At larger discharges 8.02 had larger concentrations. This is in contrast to the FDC curves, which showed that 8.01 and 8.02 had similar larger discharges (Figure 22). The larger concentrations for 8.02 for the same discharges resulted in the higher position of the 8.02 curve. The C-Q regression for 8.03 was generally high and flat compared with the other two seasons (Figure 23), and was the reason for the flat CDC in Figure 24. The graph shows, for example, that NO_3-N concentrations exceed 10 mg/L about 3% of the time for season 2, but only exceed 10 mg/L about 0.03% for season 1. The 8.01 and 8.02 comparison again shows the importance of considering seasons. The concentration of NO_3-N never exceeds10 mg/L for season 3 (8.03).

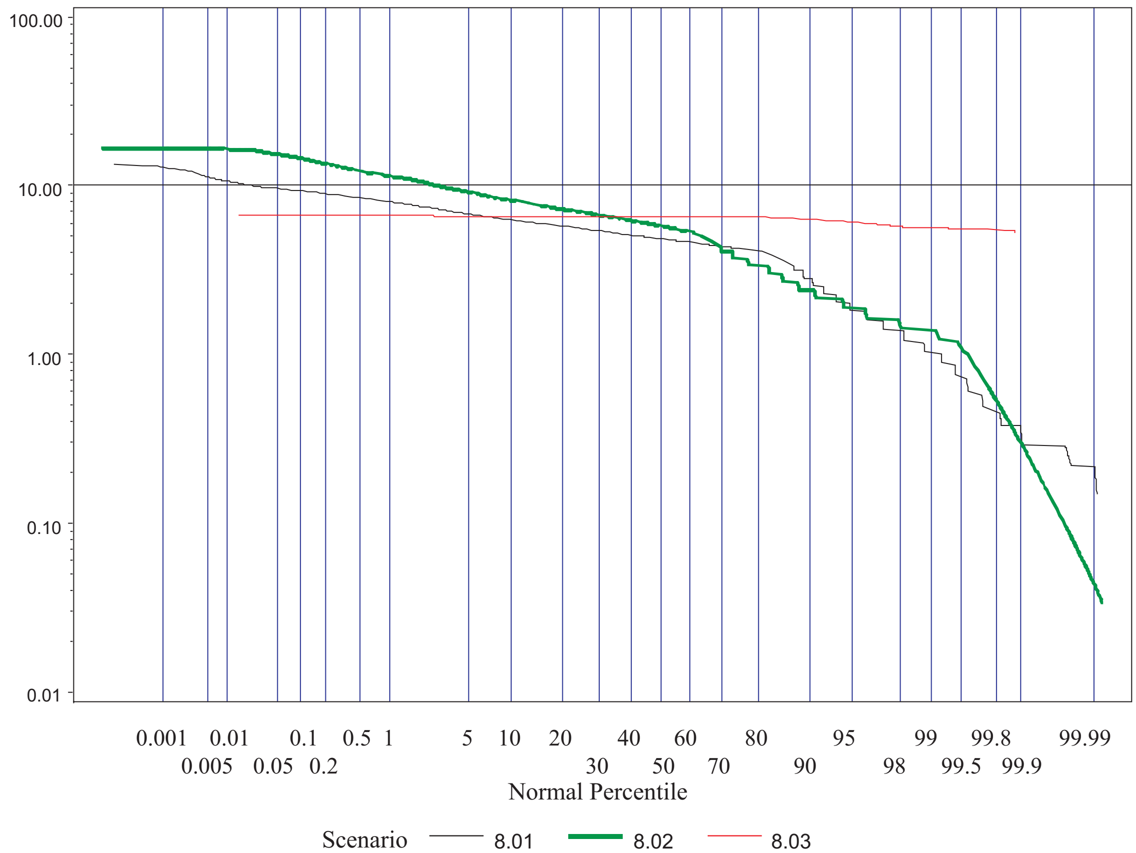

Figure 24. Concentration-duration curve for the three periods (seasons) of scenario 8 computed from regression equations.

Raw data were superimposed on the computed CDC lines to show that the CDCs developed from regressions are representative of trend of points if only the raw data were used (Figure 25). The advantage of extrapolation using the equation at the extremes is also apparent where there are no data for these infrequent wet and dry periods. The points in Figure 25 were plotted at the same exceedance level as the associated sampled discharge on the FDC.

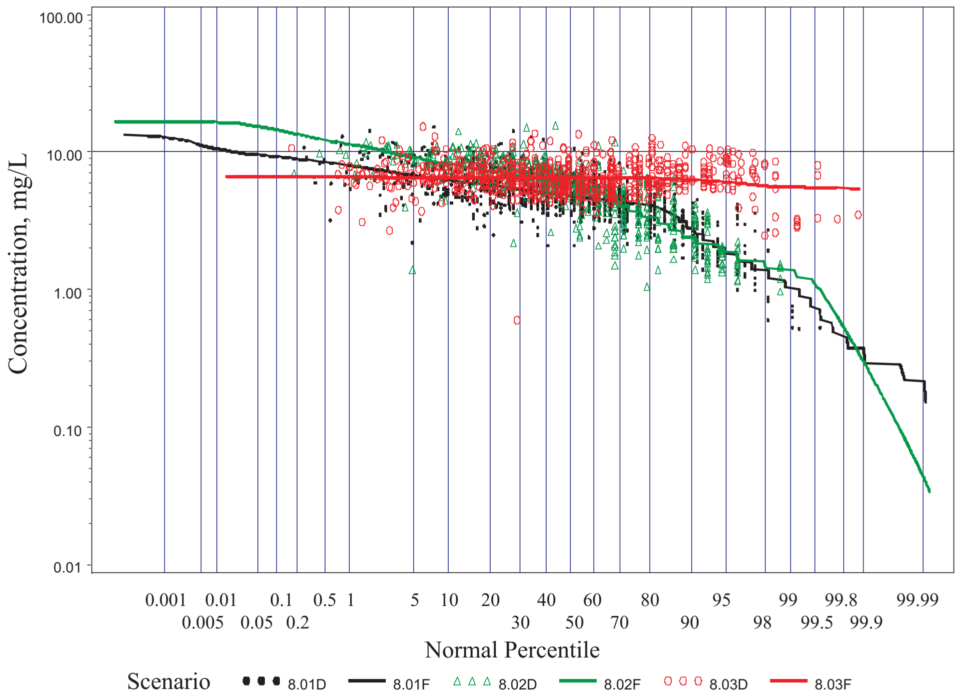

Figure 25. Concentration-duration curves and superimposed data for the three periods (seasons) of scenario 8.

<u>LDCs for seasonal data</u>

LDCs developed from the seasonal regressions and FDCs (Figure 26) show that load rates are similar for large flows for all three seasons, but 8.03 has larger load rates compared with the other two seasons for smaller load rates. The other two seasons are very similar at smaller load rates.

The LDCs with data superimposed (Figure 27) show that the LDCs computed with the FDC and regressions are representative of the central trend of the raw data. Note that the curve for 8.03 follows the nonlinear trend of the data at the small load rates. Assuming extrapolation is valid, the LDCs will provide an estimate of load rates at the extremes where sample data were not collected but where there is a more extensive discharge record.

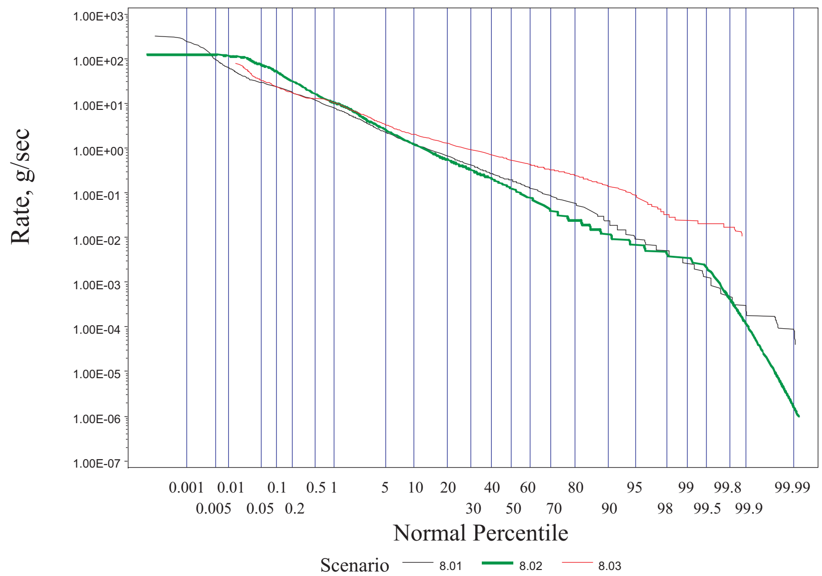

Figure 26. Load-rate-duration curve for the three periods (seasons) of scenario 8.

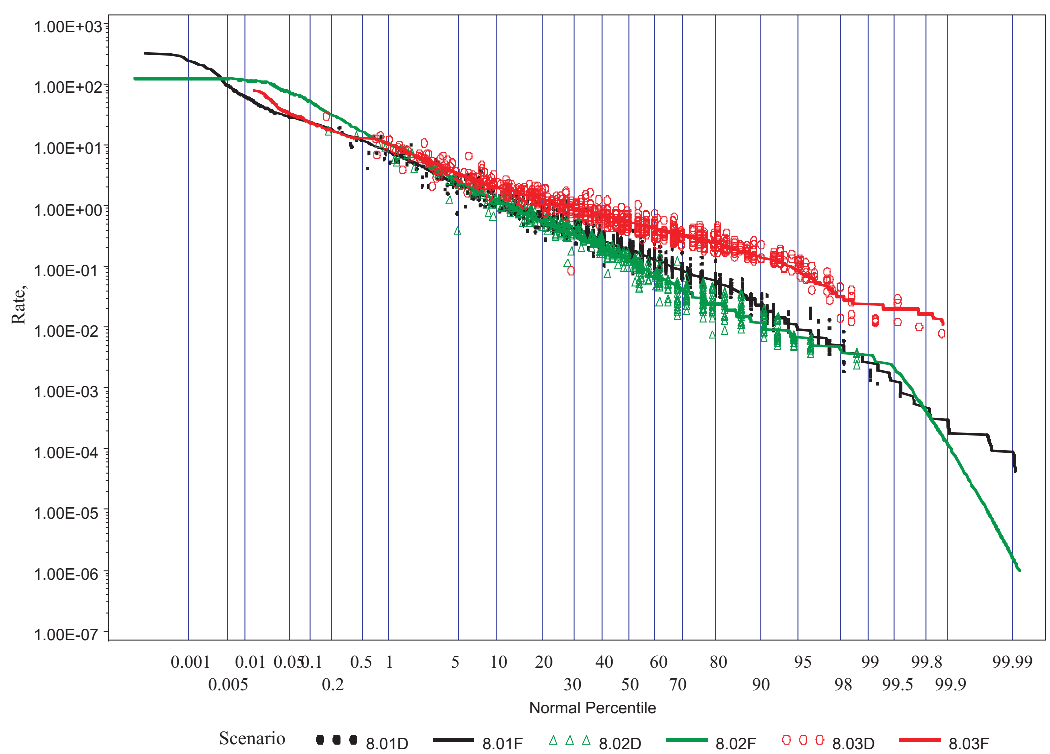

Figure 27. Load-rate-duration curves and superimposed data for the three periods (seasons) of scenario 8.

Apparent Changes in Annual Concentration-Discharge Records (Scenario 9)

The previous two sections used duration curve concepts to investigate the separation of watershed water quality and hydrology into seasons, either arbitrarily assigned or determined from data. In this section, DCs are developed after inspection of the raw water-quality data to identify periods when there are apparent changes in watershed response to precipitation. Seasons are not considered. The cause of the differences is unknown, but the different data sets show how a watershed could respond when, for example, a best-management practice(s) is implemented in the watershed.

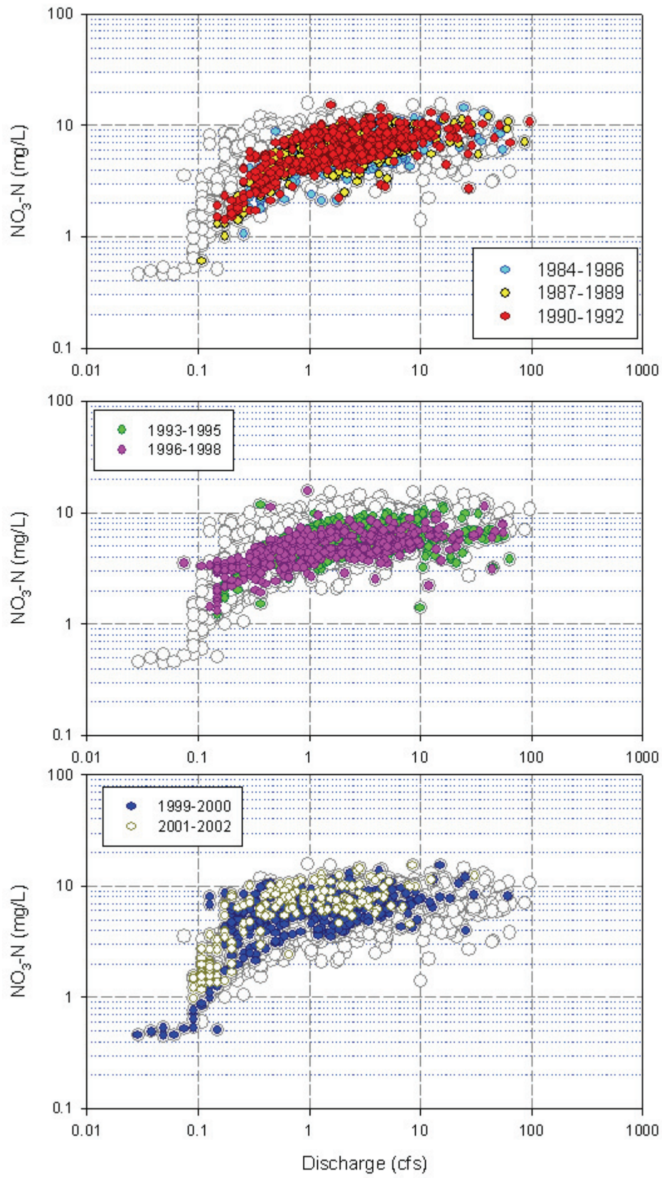

Figure 28. Concentration-flow-rate graphs for NO_3-N for each year to identify periods of similar relationships for scenario 9. Open circles depict the remainder of the data set in each graph for comparison purposes.

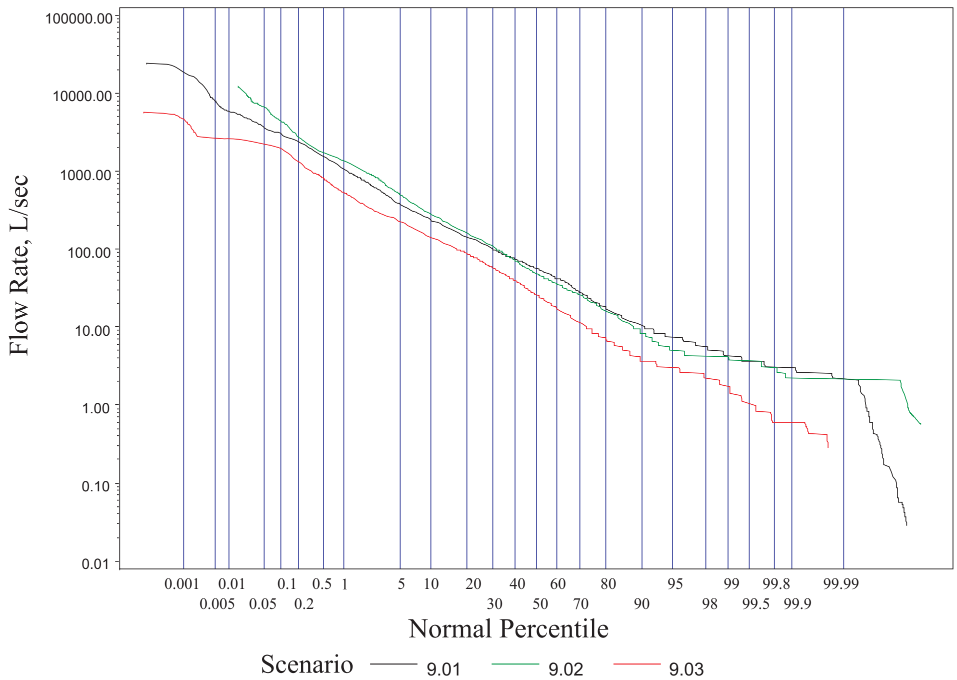

Figure 29. Flow-duration curve for the three periods of scenario 9.

Figure 28 shows plots of C-Q data for WE38 for different years. Years are grouped by visual inspection of similarity of plots, and are subsequently used in analyses. The FDCs for the three periods (Figure 29) show that periods 1 and 2 are similar, while period 3 has noticeably lower flow rates.

<u>C-Q regressions for annual periods</u>

Piecewise regressions for the three periods are presented in Figure 30 and Table 6. Generally, period 3 shows larger concentrations for similar flow rates, particularly at smaller flow rates. Periods 9.01 and 9.02 show mixed results – 9.02 has larger concentrations at smaller discharges, while 9.01 has larger concentrations at larger discharges. The intersecting discharge is similar for 9.01 and 9.02 but much smaller for 9.03 (Table 6). Regression parameters *c* and *d* are similar for 9.01 and 9.03 for the larger flows.

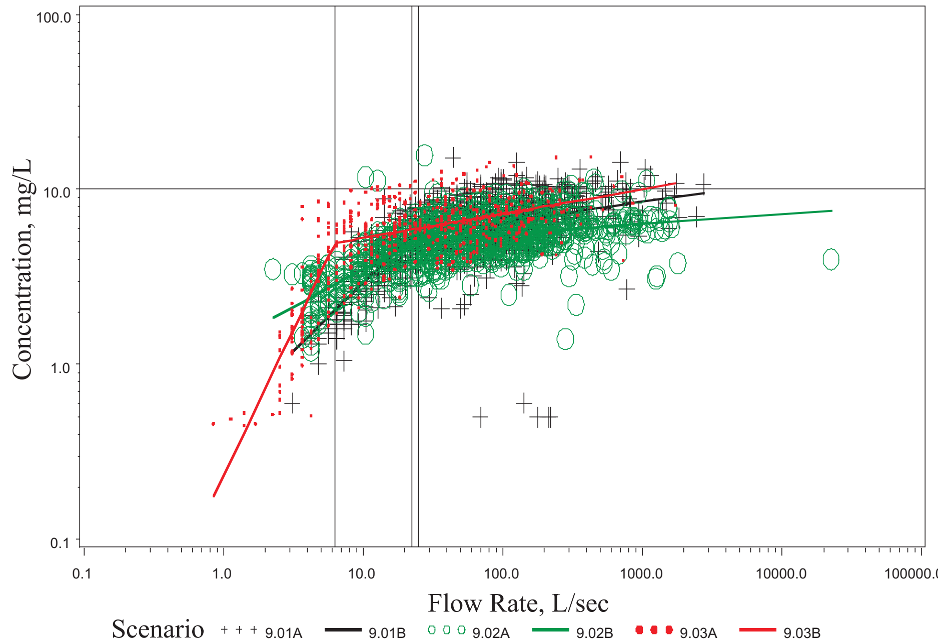

Figure 30. Piecewise-linear concentration-flow rate regressions for the three periods for scenario 9 for NO_3-N.

Table 6. Concentration-flow rate regression parameters for a 2-equation piecewise fit using the form of equation 2 for scenario 9.

	Eqn 2 Parameters*				
	Smaller Flows (<Q_i)		Larger Flows (>=Q_i)		
Scenario.Period	*a*, L/sec	*b*	*c*, L/sec	*d*	Q_i, L/sec
9.01	0.49	0.78	3.78	0.12	22.4
9.02	1.29	0.43	4.38	0.05	25.1
9.03	0.23	1.66	3.83	0.14	6.3

*Parameters *a* and *b* are for the lower flows, and *c* and *d* are the equivalent parameters for larger flows.

<u>CDCs for annual periods</u>

Unlike the FDCs for the three periods, the CDCs for periods 9.01 and 9.03 have similar concentrations at the larger flow rates, while period 9.02 has smaller concentrations (Figure 31). A comparison between relative positions of the FDCs and CDCs shows that DCs can separately account for flow regime and concentration-flow relationships, and that both of these DCs can affect the quantification of durations of concentrations in a watershed. At the low flows, 9.03 has noticeably smaller concentrations due to the lower small flows in Figure 29. The CDC for 9.02 is larger than that for 9.01 because of the relative position of the FDCs and C-Q regressions. Figure 32 shows the raw data superimposed on the CDCs, and again shows the representativeness of the computed CDCs.

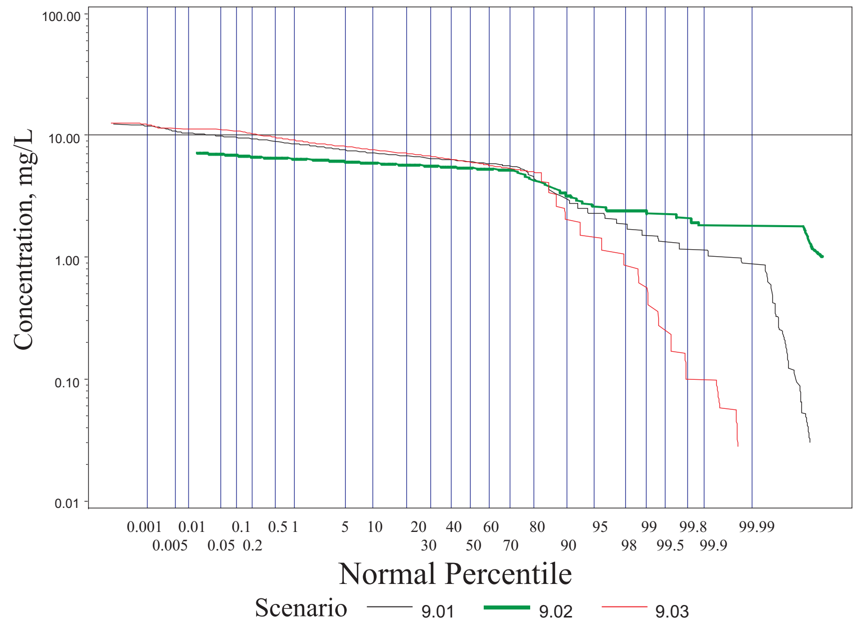

Figure 31. Concentration-duration curve for the three periods of scenario 9.

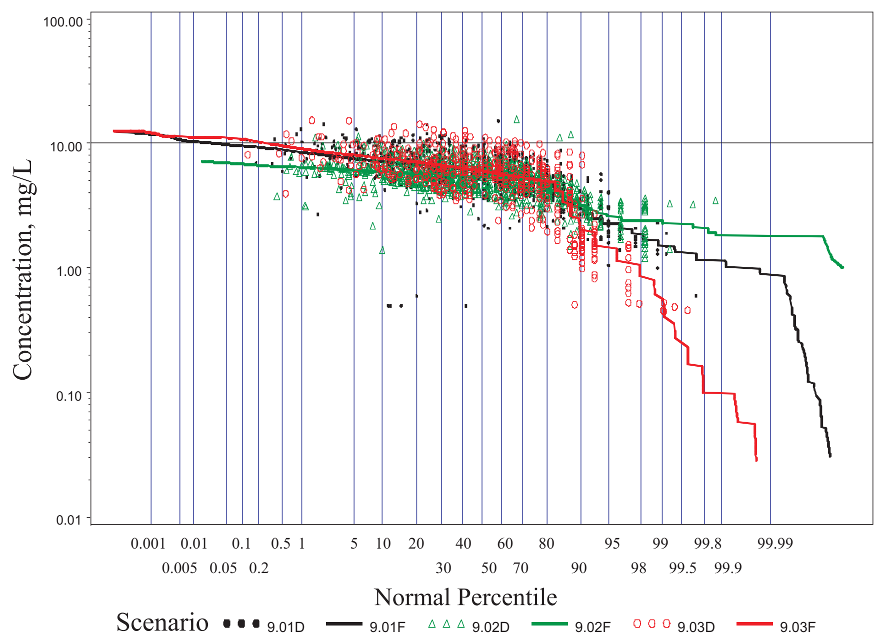

Figure 32. Concentration-duration curves and superimposed data for the three periods of scenario 9.

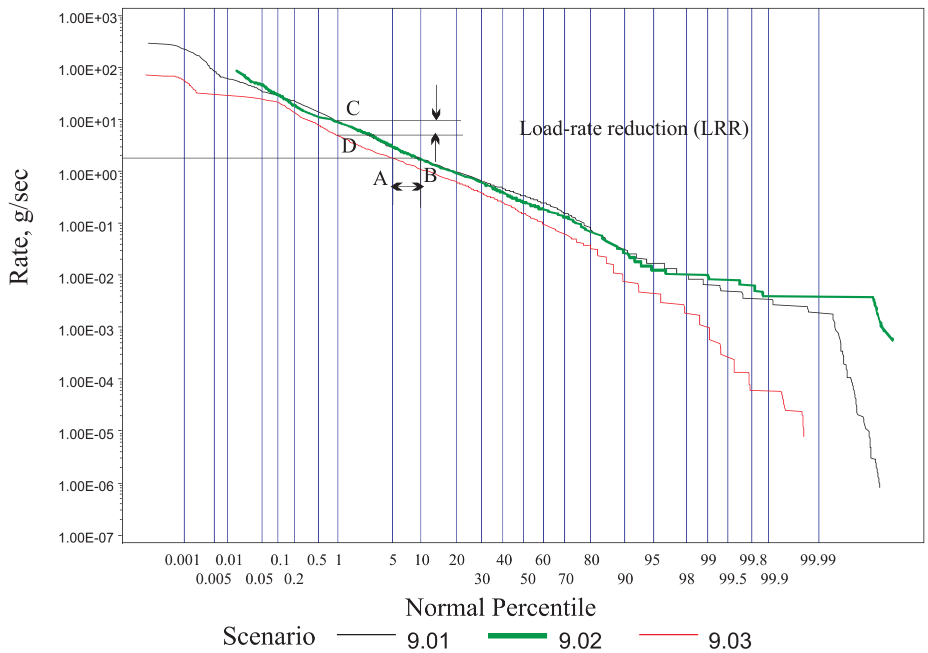

Figure 33. Load-rate-duration curve for the three periods of scenario 9.

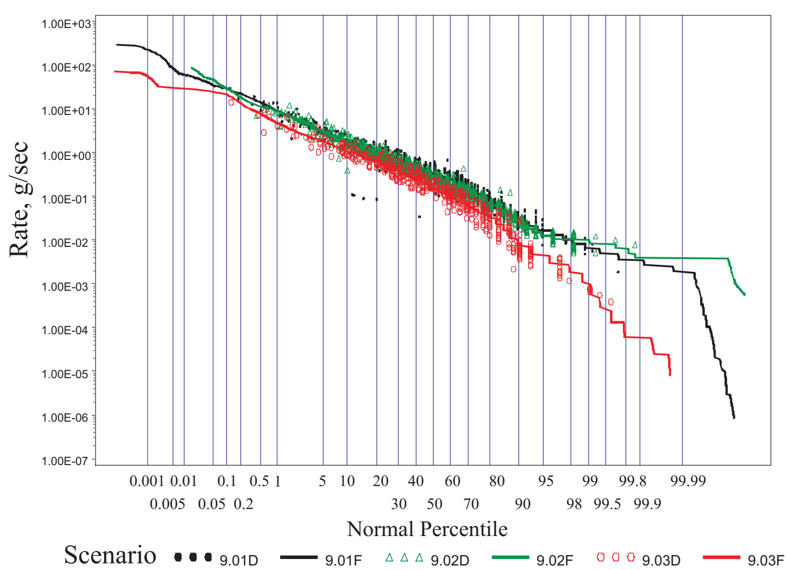

Figure 34. Load-rate-duration curves and superimposed data for the three periods of scenario 9.

LDCs and an illustration of quantifying changes in watershed conditions

The LDCs for annual periods (Figure 33 and Figure 34) show the same relative positions as the FDCs, with period 9.03 having lower load rates. Figure 33 illustrates how, by using WE38 data, DCs can be used to quantify improvements in water quality by either a reduction in exceedance (ER) or a reduction in load rate (LRR) if a management change is implemented on a watershed, and follows the presentation of the concept in Figure 8. Assume that a management change was implemented during period 9.03 from baseline conditions in period 9.02. At point B during the baseline condition, the exceedance of 10% at a load rate of 1.9 g/sec was reduced in half to point A at 5% due to the assumed management change from 9.02 to 9.03. Similarly, at an exceedance level of 1% (point C), the load-rate was reduced in half from 10 g/sec to 5 g/sec at point D due the assumed management change. Assuming that there was a management change from 9.01 to 9.02, the ER and LRR for this change in management was 0 for both variables at the same levels just discussed. This demonstrates how DCs can quantify the improvement in risk reduction and load rates. This is in contrast to computing a change in average for an entire flow range which may mask subtle changes for which a watershed manager could receive credit if a management change had been implemented. DCs provide a method to quantify changes in different parts of the flow regime.

The same concept applies to CDCs (Figure 32). However, concentrations are what are measured in the stream channel, but the regulated quantity is the load rate. DCs provide a simple method for converting concentrations to loads.

Case Study Conclusions

The following conclusions can be made from the case study using WE38 hydrology and water-quality data:

- Concentration-discharge (C-Q) correlations and regression forms of NO_3-N vary with season.
- Subdividing annual runoff and water quality data into seasons is important for identifying and quantifying natural processes affecting these variables, for constructing DCs, for detecting changes in watershed response to precipitation, following land-management changes, and for regulatory purposes.
- CDCs and LDCs developed from regressions and FDCs follow the central trend of measured data in which there can be much variability, and are useful for characterizing the constituent response over the entire range of measured flows.
- C-Q regressions in conjunction with FDCs allow extrapolation of limited data to extremes of measured flow rates (low and high flows). Obtaining a field sample at the largest flow rate may not be likely and extrapolated values may be the only way to estimate the concentration at the infrequent flows, particularly important in sampling programs of short duration.
- DCs can be used to identify seasons of year during intervals when flow and water-quality conditions are similar.
- DCs separately account for changes in watershed hydrology through the FDC and

water quality through C-Q regressions. This result suggests opportunities to estimate constituent transport and concentrations, and hydrology separately for ungauged basins.

- The simple duration-curve methodology can be used to quantify the load-rate reduction (decrease in load rates [and concentrations]) and exceedance reductions (the reduction in the percent of time a given concentration is exceeded, or reduced risk) due to a land-management change.
- LDCs developed from instantaneous data must be integrated over time (e.g., daily) to aide in TMDLs assessments. This can be accomplished by using the finding in this report that FDCs developed from average daily flows and instantaneous flows are nearly identical for mid- to low flows. However, there is a disparity at higher flows.

Report Conclusion and Summary: The Utility of Duration Curve-Based Methods

Watershed managers are faced with significant challenges when it comes to assessing the condition of water resources with respect to hydrology, ecology and water quality. The challenge becomes acute when managers are asked to quantify or predict changes in condition, and to link change to specific management actions. Simple tools that can clearly depict the condition of water resources *and* quantify change are extremely valuable. Duration-curve based methods fit this description and, along with other methods such as watershed models, GIS-based analysis, indices and multivariate statistical methods, add to the set of analytical tools available to watershed managers and other decision-makers. Duration curves can help to maximize the information in available data and provide a quantitative measure of watershed hydrology and water quality. The DC method can provide a representation of the current stream or watershed condition and, by using expected reductions in concentration or a desired water quality standard, can depict future watershed land-management scenarios. The DC method has the potential to quantify the magnitude of change in stream-water-quality characteristics after a land-management change in terms of load reduction and the reduction in the risk of exceeding selected water-quality levels. Duration-curve based methods require further investigation of how regression parameters for concentration-flow regressions change for changing land use (Bonta and Dick 2003, Bonta 2005). The DC method has untapped potential for: 1) allocating the sources of flow and chemical constituents in the watershed through the concept of mixed distributions; 2) quantifying the frequency distributions of individual durations of flows, concentrations, and loads that will facilitate setting regulated concentrations and loads for selected biological species; 3) evaluating the outputs of watershed models; and 4) understanding and quantifying the physical, climatic and hydrologic variables that contribute to watershed flow condition and water quality. The investigations pursued in this report represent a continuing evolution of duration-curve based methods. They include the following:

- The use of regression relationships with CDCs and LDCs, and the minimum number of samples needed to construct stable curves can be estimated, but needs further study for more and different types of water quality constituents.

- Flow-averaging and the time step used in constructing FDCs can affect the structure of DCs, especially for extreme low and high-flow conditions.

- The construction of, and comparison between, curves based on monthly and seasonal data can add value to an analysis because of changes in the underlying relationship between flow and concentration for a given constituent. Regression relationships may, for example, be stronger during certain times of the year (e.g., relating to fertilizer application). Stronger, more significant relationships between flow and concentration yield less uncertainty and a greater likelihood of detecting changes in condition due to management practices or other change in watershed condition.
- Examination of changes in annual data for consecutive time periods using duration-curve based methods can be used to quantify changes in concentration and load rate, but questions of uncertainty still need to be more fully addressed.

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