Ammonia Toxicity Model (AMMTOX, Version 2)

A Tool for Determining Effluent Ammonia Limits

Conceptual Background and Technical Basis

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Preface

The original version of the Ammonia Toxicity Model (AMMTOX, Version 1) was developed in 1992 by the Center for Limnology at the University of Colorado. It is patterned after the Colorado Ammonia Model (CAM), and both models operate on the premise that the toxicity of a given ammonia discharge can increase downstream of the outfall. The new model, AMMTOX Version 2, is a tool for standardizing the implementation of water quality criteria for ammonia in a manner that should make the wastewater permitting process more predictable for dischargers and regulators; with a given set of input conditions, any party should be able to run the model and obtain the same effluent limits. The model also can help provide focus for discussions about the importance of key assumptions and the potential value of additional monitoring data.

Although the intent of the model has not changed, the form and function of the model have evolved substantially. Changes have been made to accommodate a major change in the National Criteria and a new computational environment (now Excel 2000 instead of Lotus release 2). Water quality criteria for ammonia have changed over time to reflect improved understanding of the sensitivity of aquatic organisms to the toxicity of total and unionized ammonia. For many years, toxicity was defined solely in terms of unionized ammonia (USEPA 1985). The recent National Criteria document (USEPA 1999) concludes that a joint toxicity model, defined in terms of total ammonia, is required. The full text of the National Criteria document, Federal Register notices, and fact sheets are available at the following web site: http://www.epa.gov/ost/standards/ammonia/.

The need to make changes also created an opportunity to revamp the design of the model. In part, the revision consists of a simplification that combines the many spreadsheets required for operation of the previous version. The more important change consists of a segregation of tasks and a more realistic representation of conditions in the stream below the outfall.

The revision of AMMTOX has benefited from recent work on CAM and from more than a decade of practical experience with permitting and TMDL issues in Colorado. In addition, perspectives gained at the recent National Permit Writers Workshop sponsored by EPA in Denver, CO (December 2001) have been useful in understanding issues confronted by regulatory agencies in other states. Many individuals have been helpful in the development of AMMTOX. In particular, we would like to acknowledge Dennis Anderson, John Farrow, Lynn Kimble, Eric Oppelt, and Bob Owen of the Water Quality Control Division at the Colorado Department of Public Health and Environment, and Bruce Zander of USEPA Region VIII. Development of AMMTOX Version 2 has been supported by project award X988303-01.

Introduction

Setting NPDES permit limits for ammonia is complicated by two factors that do not play a role for most pollutants: non-conservative behavior and control of toxicity by environmental variables. For most pollutants, toxicity depends only on the concentration of the pollutant. NPDES limits can be computed using a simple mass balance equation to find the effluent concentration that, when added to the receiving water, will yield a mixed concentration that matches the stream standard. The procedure is simple because the controlling condition (the location at which highest concentration occurs) is just below the outfall.

When toxicity is controlled by factors in addition to the concentration of the pollutant, the possibility arises that the controlling condition will be displaced some distance downstream from the outfall. The toxicity of ammonia is strongly influenced by two environmental factors, pH and temperature, both of which may exhibit substantial spatial and temporal variation in streams. Spatial variation in pH and temperature occurs naturally in streams, but an important pattern may be introduced through the addition of effluent to a stream.

The pH and temperature of an effluent rarely match those in the receiving water. In particular, effluent pH is almost always lower than stream pH. When effluent is mixed with stream water, the temperature of the mixture is altered and the pH is depressed. Changes in pH and temperature alter the toxicity of a fixed concentration of total ammonia. If pH and temperature remained constant at the mixed conditions, the controlling condition would remain just below the outfall, but they do not remain constant. PH and temperature in the stream will tend to shift to an equilibrium set of conditions over distance (=time). The rise in pH that is characteristic of the mix of effluent and stream water typically results in increasing ammonia toxicity downstream.

A spatial pattern of increasing toxicity downstream of an outfall would be an inconvenience when establishing limits for a conservative pollutant because mass balance calculations at the outfall must be supplemented with predictions of toxicity over distance. The problem is relatively minor, however, as long as the concentration of the pollutant remains constant. Once the controlling condition for toxicity is defined, the calculation of permit limits proceeds as if that condition occurred at the outfall.

Ammonia does not behave conservatively in streams. It is an important source of nitrogen for algae and is the substrate for nitrifying bacteria. The concentration of ammonia can be diminished very rapidly in response to biological demand. Whenever the controlling condition for toxicity is displaced some distance below an outfall, reduction in ammonia concentration alters the basis for setting permit limits.

The process governing the downstream increase in toxicity operates independently of the biological processes reducing the concentration of ammonia. The interaction of these two mechanisms will tend to shift downstream the point at which aquatic organisms are at greatest risk. Prediction of the controlling condition for the permit depends on the outcome of nonlinear processes that can only be assessed with a model.

There is a need for a modeling framework that incorporates relevant processes in a manner that is intelligible to dischargers and regulators, and is relatively easy to use. The tasks that must be accomplished with the model include: 1) definition of temporal patterns of ammonia toxicity in the receiving water, 2) determination of the threshold for exceedances (e.g., once in three years), 3) definition of spatial patterns of ammonia toxicity downstream of the outfall, 4) location of the controlling condition, and 5) connection of permit limits to stream standards applicable at the controlling point. Controlling conditions are characterized through a recurrence analysis that relies chiefly on grab sample data,

supplemented by local or regional knowledge of patterns of variation in key variables. A mass balance model, which defines longitudinal changes in water quality, creates the basis for setting permit limits. A graphical representation of downstream changes in ammonia makes it possible to incorporate multiple dischargers. For a given set of inputs, anyone should be able to run the model and obtain the same output. This provides a predictable environment for dischargers and regulators. It also focuses attention on the quality of critical data or the most important information to obtain in the future.

This manual describes the concepts behind AMMTOX and serves as a practical guide to its use. It begins with an overview of the new National Criteria and a discussion of issues related to implementation. The next section explains the importance of temporal variation in toxicity and how that is relevant to the definition of standards. A third section defines the modeling concepts associated with the downstream displacement of the controlling condition and explains the data needed for the assessment. A companion document is devoted to operation of the model, including sources for input conditions.

Stream Standards

The effects of pH and temperature on the toxicity of ammonia are incorporated in equations that define stream standards for total ammonia (USEPA 1999). If pH and temperature were constant in streams, it would be an easy matter to calculate the appropriate standard, but both constituents vary on time scales that are important for setting standards. Because the equations defining ammonia toxicity are nonlinear, a standard calculated from the average pH and average temperature is not the same as the average of a set of standards calculated from individual pH and temperature values. A significant challenge for AMMTOX is to capture the natural variability of pH and temperature in a manner that can be applied to the calculation of stream standards.

Regulatory Basis

Ammonia in surface waters occurs in two forms, ionized (NH_4^+) and unionized (NH_3), both of which contribute to the toxicity of ammonia to aquatic organisms (USEPA 1999). Present standards are based on a joint toxicity model that incorporates the contributions of both forms. The ionic composition of the receiving water also is thought to play a role in determining the toxicity of ammonia, but is not included in the National Criteria because the contribution is not well understood and is not thought to be important for most fresh waters (USEPA 1999).

The acute standard (Criterion Maximum Concentration, or CMC) defines a one-hour average concentration that should not be exceeded more than once in three years, on average. Acute toxicity is a function of pH, and separate standards have been developed depending on the presence or absence of salmonids. Temperature does not affect the CMC. In the absence of salmonids, the CMC is about 50% higher (i.e., less restrictive) than the CMC in the presence of salmonids (Figure 1), reflecting the ratio of the Final Acute Values (FAV) at a pH of 8 (16.8 without salmonids and 11.23 for large rainbow trout).

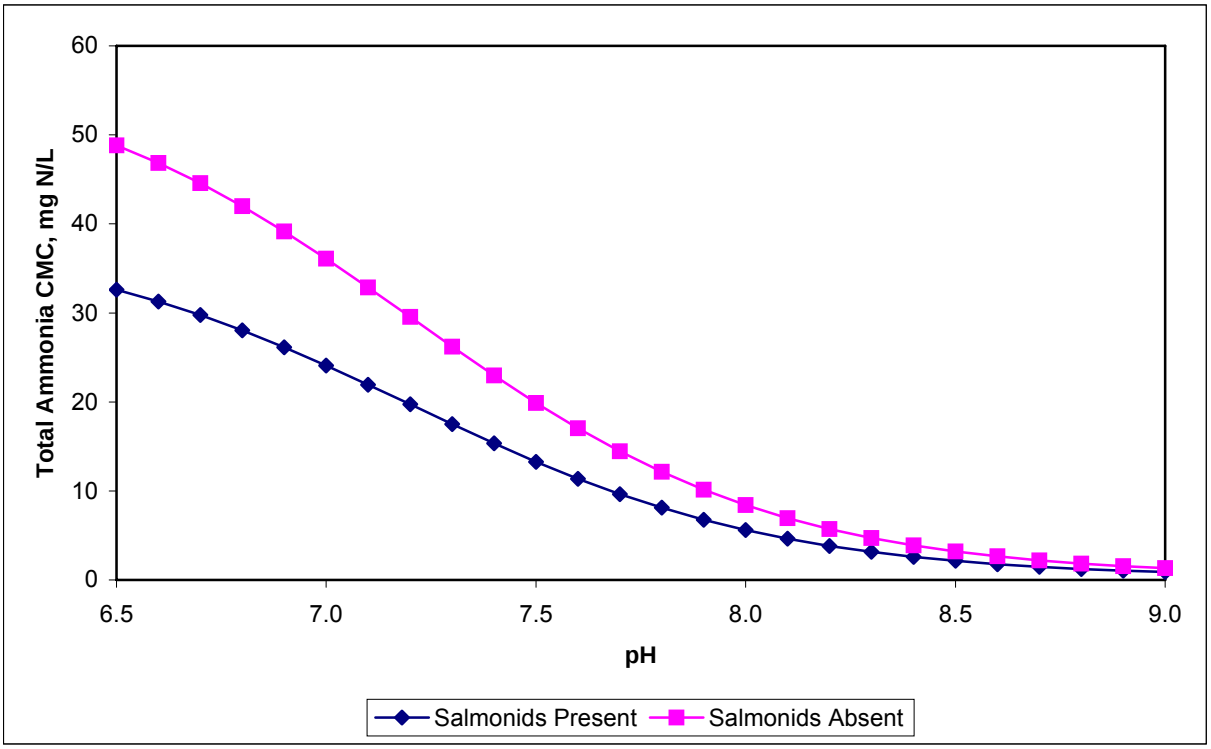

Figure 1. Total ammonia CMC defined as a function of pH. CMCs are more restrictive when salmonids are present. Symbols represent pH increments of 0.1 units used to create the curves.

The chronic standard (Criterion Chronic Concentration, or CCC) applies to a 30-d averaging period, and it also is a concentration that should not be exceeded more than once in three years, on average. Temperature and pH affect the chronic standard. The pH component of the CCC has the same form as that of the CMC, but uses different constants. Separate equations have been developed for the temperature component depending on the presence or absence of early life stages (ELS) of fish (Figure 2). At all temperatures, invertebrates are more sensitive to ammonia than are the older life stages of fish. The function derived for invertebrates (*Hyallela*) is nonlinear above 7°C and constant below 7°C. When ELS are present and the temperature is less than 14.5 °C, the Genus Mean Chronic Value (GMCV) of *Lepomis*, which does not vary with temperature, controls the temperature term.

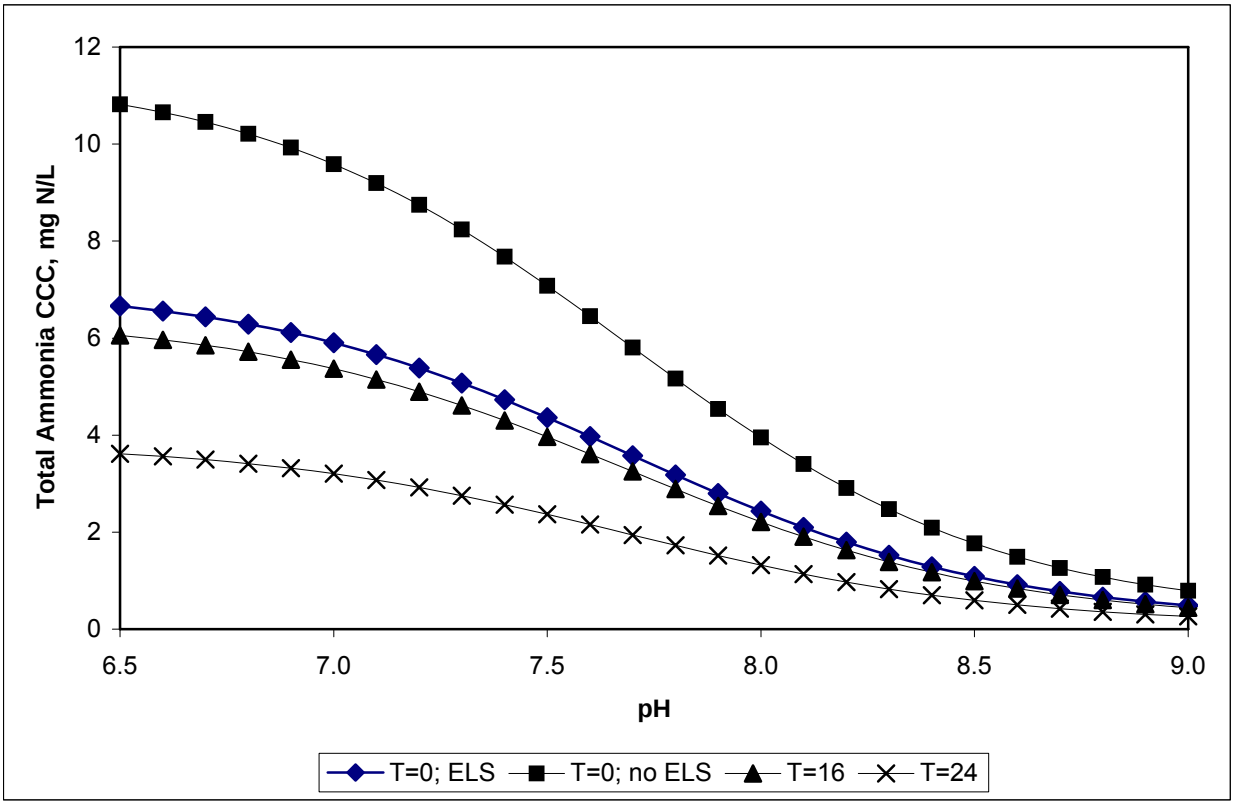

Figure 2. Total ammonia CCC defined as a function of pH. CCCs are more restrictive at low temperatures when ELS are present; there is no difference when temperature exceeds 14.4°C. Symbols represent pH increments of 0.1 units used to create the curves.

Although the chronic criterion (CCC) is defined explicitly for a 30-d averaging period, it is also subject to an additional constraint: "…the highest four-day average within the 30-day period should not exceed 2.5 times the CCC" (USEPA 1999). It is of considerable importance to the modeling strategy to know which of the two averaging periods is likely to control the calculation of limits in most situations. The problem was investigated using an approach developed in the Technical Support Document for Water Quality-based Toxics Control (USEPA 1985). The limits depend in part on the number of observations made during the month. Although the approach was defined specifically for setting effluent limits, it is applicable to a steady-state model of stream concentrations. The approach assumes a lognormal frequency

distribution for concentration; equations are defined for calculating average daily (monthly) limits for 95th and 99th percentiles.

It is assumed that the true value of the mean (long-term average; LTA) and the coefficient of variation (CV) of the underlying distribution are the same whether the number of observations is 4 or 30. In addition, it is assumed that observations are independent. The 95th (or 99th) percentile for the average daily limit based on 4 observations is compared to that based on 30 observations (Table 1). The ratio of the two limits varies nonlinearly with the CV, but is independent of the LTA. In no case is the ratio as high as the threshold of 2.5 specified in the criterion. If the underlying distribution is assumed to be normal instead of lognormal, the ratio is more responsive to changes in the CV. When the CV exceeds 15 (i.e., 1500%), the ratio of the average daily limit with 4 observations to that with 30 observations will exceed 2.5. It is reasonable to conclude that modeling based on a 30-d interval will be appropriate for setting limits with a steady-state model. Compliance with the 4-d CCC should be checked in the field.

	Average Daily Limit (N=4)		Average Daily Limit (N=30)		Ratio of limits	
CV	P= 0.95	P= 0.99	P= 0.95	P= 0.99	P= 0.95	P= 0.99
0.5	5.8	6.9	4.6	4.9	1.257	1.398
1.0	7.8	10.7	5.3	6.0	1.468	1.790
2.0	11.1	19.6	6.7	8.6	1.655	2.293
5.0	15.0	39.3	10.6	18.1	1.415	2.172
10.0	15.3	52.3	14.1	32.1	1.085	1.626

Table 1. Comparison of average daily limits based on 4 and 30 observations, for 95th and 99th percentiles. The underlying distribution is assumed to be lognormal with a long-term average concentration of 4.

The form of equations presented in the National Criteria document has been altered to allow flexibility in the selection of constants in the event AMMTOX is used in conjunction with site-specific ammonia criteria. Explanations of the equations and terms used in AMMTOX are given in Appendix A.

Modeling Concept – Coping with Variation

Stream standards for ammonia are calculated from nonlinear relationships that account for the dependence of toxicity on environmental conditions; the acute standard is calculated based on pH, and the chronic standard is calculated from pH and temperature. If pH and temperature were constant, it would be a simple matter to calculate the corresponding standard. In most natural streams, however, pH and temperature change continuously. Significant temporal variability is apparent on daily and seasonal time scales for pH and temperature in most surface waters. The variability is not random; it conforms to specific patterns that are predictable.

Diel variation in stream temperature has been studied extensively and the daily pattern can be described with a sine function. The pattern of temperature variation is explained by the 24-h cycle of heat exchange, which typically produces a maximum temperature in late afternoon and a minimum temperature near dawn (Figure 3). The amplitude of variation and the time of day at which maximum temperature (t_{max}) occurs have been studied in Colorado and are remarkably constant across a wide variety of streams (Tables 2-3). The diel pattern of variation is superimposed on seasonal variation in the mean daily temperature, which is evident from trends in the daily minima and maxima (Figure 4). For modeling purposes, diel variation in temperature is sufficiently predictable that one set of general (default) values usually suffices for characterizing the time of the maximum and the amplitude of daily variation in each month of the year (Table 6). It should be noted, however, that site-specific data are always preferable to default values. Furthermore, some judgment should be exercised before accepting any

default values. For example, the daily amplitude of temperature variation probably is smaller in the largest streams (see Colorado River in Table 2) than in the smallest ones. Similarly, diel variation in temperature may be suppressed for streams where flow is dominated by a nearby reservoir release or large effluent contribution.

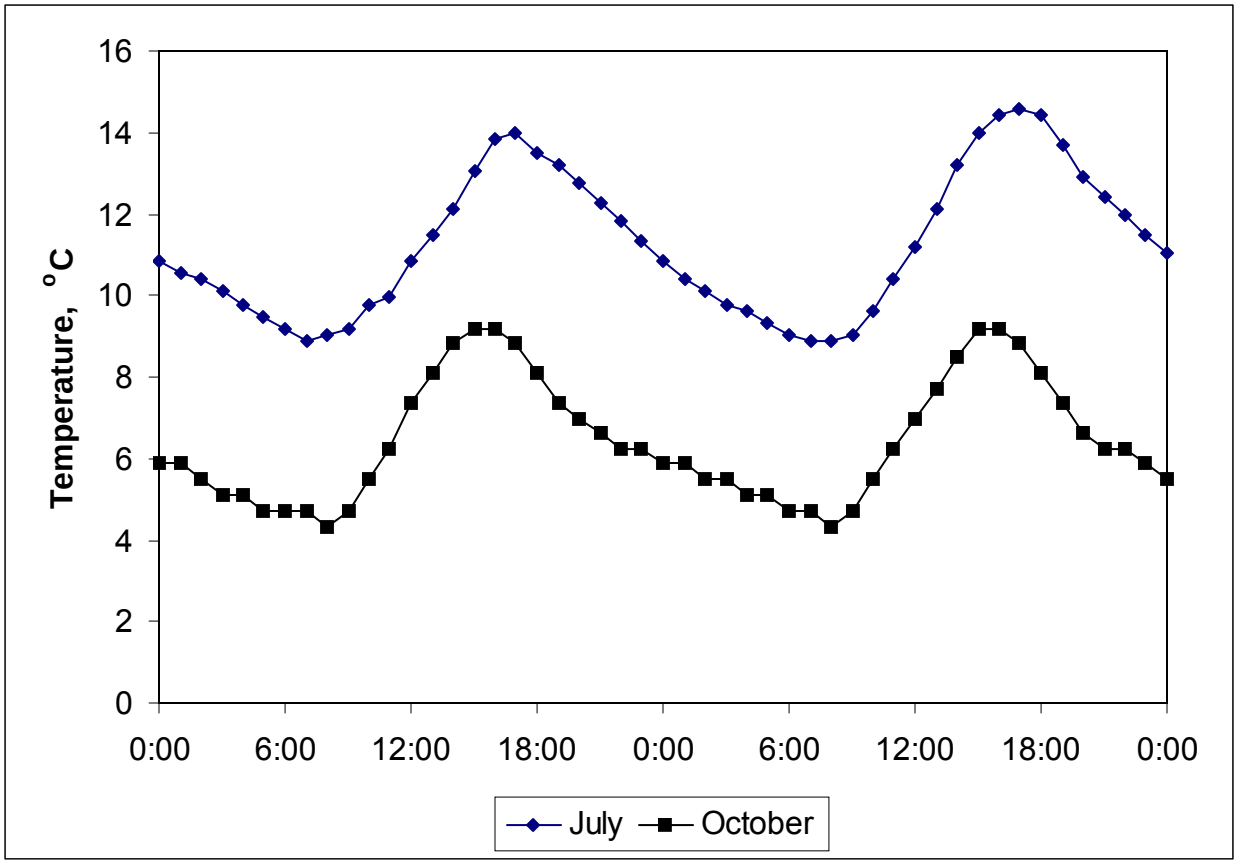

Figure 3. Hourly temperatures for North St Vrain Creek in July and October 1996 (unpublished data from J. McCutchan).

Stream	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Arkansas at Avondale	1.50	2.10	2.50	2.60	2.40	2.30	2.60	2.50	2.60	2.20	1.60	1.40
Big Thompson					4.00	3.50	3.50					
Boulder above Coal	2.78	3.10	3.50	3.97	4.31	4.47	4.38	4.07	3.62	3.18	2.83	2.68
Boulder at mouth	2.35	2.74	3.31	4.01	4.58	4.91	4.88	4.50	3.88	3.20	2.62	2.31
Cache la Poudre at Lincoln			2.00		4.00		3.00				1.00	
Cache la Poudre at Boxelder			3.00		3.00		3.00				1.30	
Coal at Louisville	2.02	2.64	3.44	4.38	5.10	5.44	5.30	4.70	3.81	2.90	2.18	1.86
Coal at mouth	1.90	2.21	2.73	3.44	4.08	4.50	4.58	4.29	3.71	3.03	2.37	1.97
Colorado at CO-UT line	0.45	0.65	0.85	0.85	0.85	0.75	0.90	0.85	0.85	0.70	0.50	0.40
Rio Grande at Alamosa											3.00	
Purgatoire at Trinidad			6.50						5.55			
South Platte at Littleton			2.75									
South Platte at Englewood	2.00	2.00	3.00	4.00	4.00	4.00	4.00	4.00	4.00	2.00	2.00	2.00
South Platte at Henderson		2.34		2.49				2.05	2.11	2.27		
St Vrain at Lyons	0.27	1.28	3.08	2.86	2.21	1.63	2.46	2.47		1.80	1.58	0.41
St Vrain below Longmont	2.78	3.09	3.47	3.91	4.22	4.36	4.27	3.97	3.54	3.12	2.80	2.68
Yampa									3.15			

Table 2. Daily amplitude of temperature variation typical for each month in Colorado streams. Data are from the Colorado Department of Health and Environment, Water Quality Control Division, or from unpublished sources used in development of NPDES permit limits.

Stream	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Arkansas at Avondale	16:00	17:00	17:00	17:00	17:30	17:30	17:30	17:00	17:00	17:00	15:30	15:30
Bear	19:00									17:00		
Big Thompson		16:00	15:00	16:00	17:00	17:00	17:00					
Boulder above Coal	15:00	15:00	15:00	15:00	16:00	17:00	15:00	15:00	15:00	15:00	15:00	15:00
Boulder at mouth			15:00		16:00	18:00	16:00	16:00	16:00	16:00	14:00	
Cache la Poudre at Lincoln			15:00		16:00						16:00	
Cherry	15:00		17:00						15:30	16:00		
Coal at Louisville	15:00	15:00	15:00	16:00	16:00	15:00	15:00	15:00	17:00	17:00	14:30	14:30
Coal at mouth	15:00	15:00	15:00	15:00	16:00	16:00	15:00	15:00	15:00	15:00	15:00	15:00
Purgatoire at Trinidad			18:00						17:00			
South Platte at Littleton	15:00		16:00						19:00	16:00		
South Platte at Englewood	15:00	16:00	17:00	17:00	17:00	17:00	17:00	17:00	17:00	17:00	16:00	15:00
South Platte at Henderson												
St Vrain at Lyons	13:00	16:00	17:00	17:00	17:00	15:00	17:00	17:00	16:00	16:00	16:00	16:00
St Vrain below Longmont			15:00		16:00	18:00	16:00	16:00	16:00	16:00	14:00	
Yampa at Steamboat									17:00			
Yampa at Hayden									18:00			

Table 3. Time of daily temperature maximum typical for each month in Colorado streams. Data are from the Colorado Department of Health and Environment, Water Quality Control Division, or from unpublished sources used in development of NPDES permit limits.

Stream	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Arkansas at Avondale	0.21	0.23	0.20	0.18	0.21	0.16	0.14	0.16	0.19	0.21	0.18	0.21
Bear	0.00									0.50		
Big Thompson		0.25	0.10	0.10	0.15	0.15	0.10					
Boulder above Coal	0.60	0.65	0.78	0.70	0.79	0.40	0.75	0.90	1.10	0.75	0.58	0.53
Boulder at mouth	0.54		0.64		0.80	0.35	0.68	0.61	0.75	0.53	0.61	
Cherry	0.00		0.45						0.05	0.20		
Coal at Louisville	0.22	0.25	0.39	0.21	0.23	0.21	0.55	0.21	0.23	0.28	0.23	0.18
Coal at mouth	0.48	0.65	0.45	0.23	0.28	0.20	0.30	0.25	0.23	0.35	0.15	0.33
East		0.15				0.00	0.15	0.10				0.00
Fountain		0.00					0.10					0.00
Gunnison						0.15		0.20				
Monument							0.10					
Piceance									0.05			
Purgatoire			0.15						0.35			
Rio Grande											0.00	
Roan								0.00				
San Miguel								0.00				
Slate							0.10					
South Platte in Denver	0.20		0.10						0.25	0.00		
South Platte at Henderson	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
St Vrain below Longmont	0.54		0.32		0.40	0.25	0.24	0.23	0.49	0.44	0.38	
Taylor						0.00		0.10				
Tomichi						0.10		0.20				
Yampa									0.15			0.00

Table 4. Daily amplitude of pH variation typical for each month in Colorado streams. Data are from the Colorado Department of Health and Environment, Water Quality Control Division, or from unpublished sources used in development of NPDES permit limits.

Stream	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Arkansas at Avondale	15:30	15:15	14:45	15:30	16:00	18:37	19:00	17:22	16:00	16:00	15:30	15:30
Bear										11:00		
Big Thompson		12:30	10:30	14:30	16:00	15:00	16:00					
Boulder above Coal	14:00	15:00	15:00	14:00	15:00	15:00	14:00	14:00	16:00	14:00	13:00	14:00
Boulder at mouth	14:00		15:00		15:00	14:00	16:00	16:00	16:00	16:00	14:00	
Cache la Poudre			14:45		15:30		16:00				14:30	
Cherry			12:00						13:00	12:00		
Coal at Louisville	16:00	16:00	16:00	15:00	15:00	15:00	14:00	14:00	14:00	15:00	15:00	16:00
Coal at mouth	14:00	14:00	15:00	16:00	15:00	15:00	15:00	14:00	14:00	14:00	15:00	14:00
East		23:00					13:00	14:00				
Fountain							12:00					15:00
Gunnison						14:00		17:00				
Monument							15:00					
Piceance									14:00			
Purgatoire at Trinidad			16:00						20:00			
Rio Grande at Alamosa											16:00	
St Vrain below Longmont			15:00		16:00		16:00	16:00	16:00	15:00	15:00	
Taylor								13:30				
Tomichi						17:00		16:30				
Yampa at Steamboat									16:00		16:00	
Yampa at Hayden									18:00			

Table 5. Time of daily pH maximum typical for each month in Colorado streams. Data are from the Colorado Department of Health and Environment, Water Quality Control Division, or from unpublished sources used in development of NPDES permit limits.

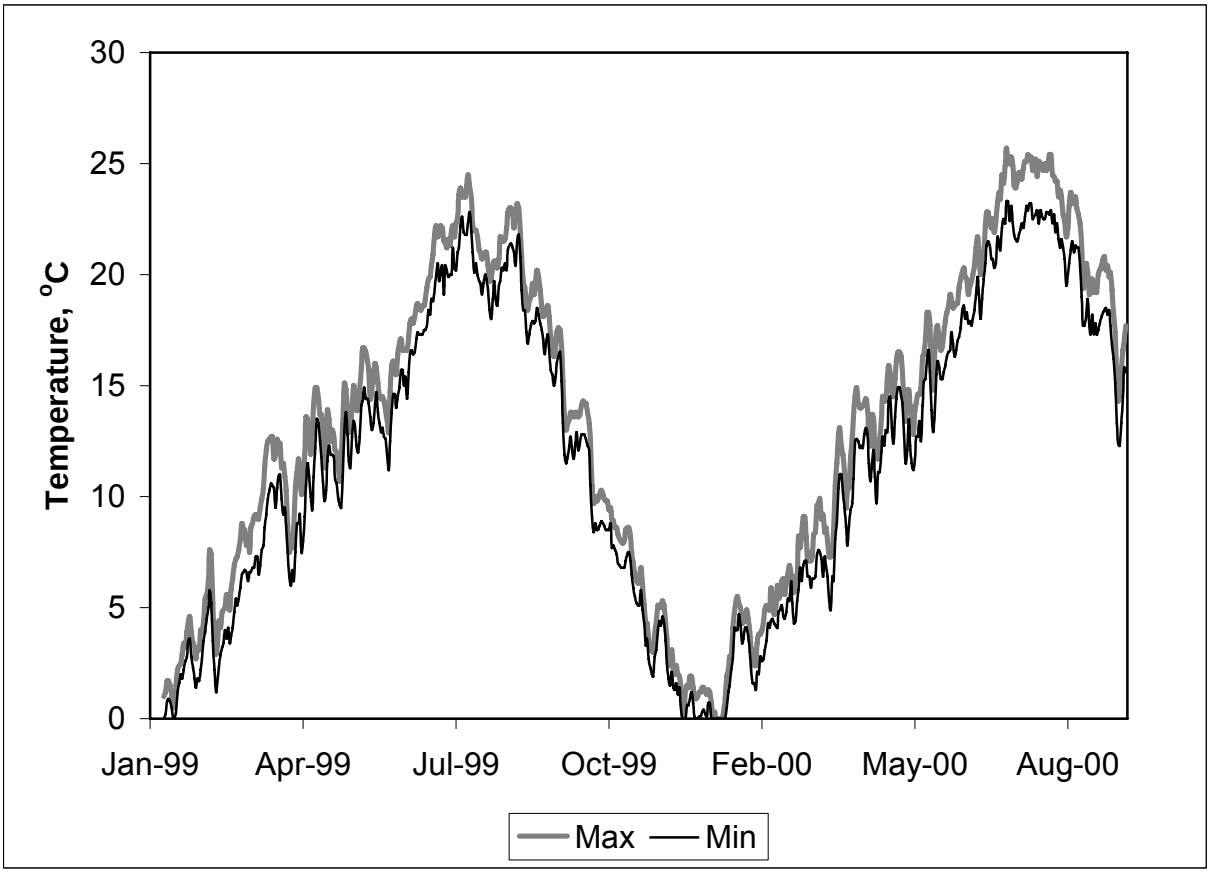

Figure 4. Seasonal variation in daily maximum and minimum temperatures in the Colorado River at the CO-UT line.

	Default pH Conditions				Default Temperature Conditions	
	Amplitude					
Month	Low	Medium	High	t_{max}	Amplitude	t_{max}
Jan	0.2	0.2	0.3	14:00	2.0	15:00
Feb	0.2	0.2	0.3	15:00	2.3	15:00
Mar	0.2	0.2	0.3	15:00	3.0	15:00
Apr	0.2	0.2	0.3	15:00	3.5	16:00
May	0.2	0.3	0.5	15:00	4.0	16:00
Jun	0.2	0.3	0.5	15:00	4.0	17:00
Jul	0.2	0.3	0.5	15:00	4.0	17:00
Aug	0.2	0.3	0.5	15:00	4.0	17:00
Sep	0.2	0.3	0.5	16:00	3.5	17:00
Oct	0.2	0.2	0.5	15:00	2.5	16:00
Nov	0.2	0.2	0.3	15:00	2.0	15:00
Dec	0.2	0.2	0.3	15:00	2.0	15:00

Table 6. Default amplitudes and times of maxima (t_{max}) describing diel variation in pH and temperature. Some smoothing has been applied to results collated from various sources.

The seasonal pattern of temperature variation in AMMTOX is created through monthly time steps, the use of which implies that routine data should be collected at least once a month. The effect of infrequent sampling on model results is likely to be greatest at the time of the annual minimum or maximum temperature. Steele's (1985) analysis of the upper Colorado River basin shows that the minimum typically occurs in mid-January and the maximum in mid-July. The absence of measured values in January, for example, would probably result in unrealistically high mean temperatures for that month because the model interpolates between values in adjacent months. If the temperature used for January were higher than really occurs, the corresponding standard would be more stringent than necessary for the month. Missing data in July would result in the opposite problem: a less stringent standard than appropriate. However, data would have to be missing for July in every year of the record for this problem to have a serious impact on model results.

PH also exhibits a strong pattern of diel variation, driven largely by biological processes. The 24-h pH cycle is explained by changes in the balance of photosynthesis and respiration as the amount of sunlight changes over the course of a day (Figure 5). Photosynthesis, which causes pH to rise as inorganic carbon is removed from the water, is dominated in many streams by algae attached to rock, gravel, or other substrates. In some streams, macrophytes or suspended algae also may be an important autotrophic component. As sunlight reaches these organisms in early morning, photosynthesis begins to drive up the pH of the stream. As the intensity of sunlight increases, the rate of photosynthesis increases, and the pH continues to rise. In late afternoon, the amount of light decreases, and both the rate of photosynthesis and the pH tend to level off and then decrease. Free CO_2 may be depleted toward midday, which will result in suppression of photosynthesis in the last half of the day. Changes in stream pH also may occur at night when respiration and diffusive gain of CO_2 in the presence of a CO_2 deficit tend to lower the pH. For these reasons, the pH of a stream typically decreases between sunset and sunrise. Respiration also occurs during the day, but its effects on pH during the day are usually masked by photosynthesis.

Within a geographical region, pH will likely show more variation among streams than does temperature because photosynthesis is subject to regulation by temperature, sunlight, and nutrient concentrations. A review of data available from Colorado supports this view, although the time of the daily maximum is relatively constant across streams (Tables 4-5). Streams that have a canopy of vegetation, as in heavily forested areas, are likely to show less diel pH variation than plains streams, which typically lack a canopy.

A sine function provides a reasonable characterization of the 24-h pattern of pH variation (Figure 6), but there is enough variation among streams that it would not be prudent to restrict the model to a single set of defaults. Consequently, three default categories have been established: high, medium, and low (Table 6). A certain amount of site-specific information during the summer months is necessary to characterize pH variation in each stream.

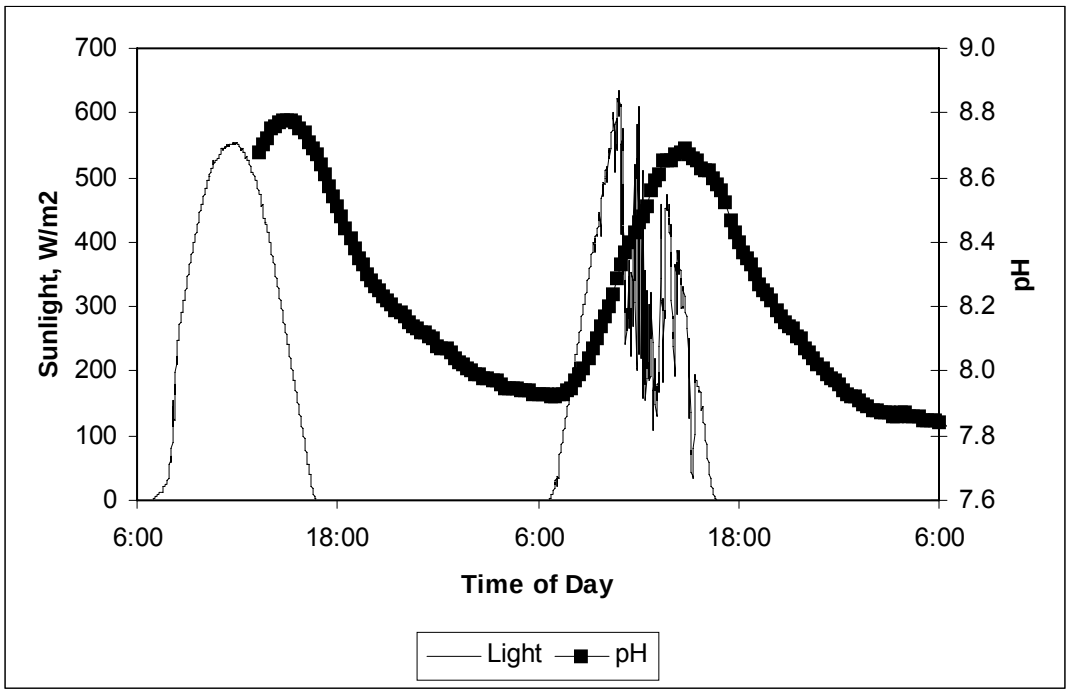

Figure 5. Diel pattern of pH in the South Platte River near Denver, November 1999. Sunlight is also shown.

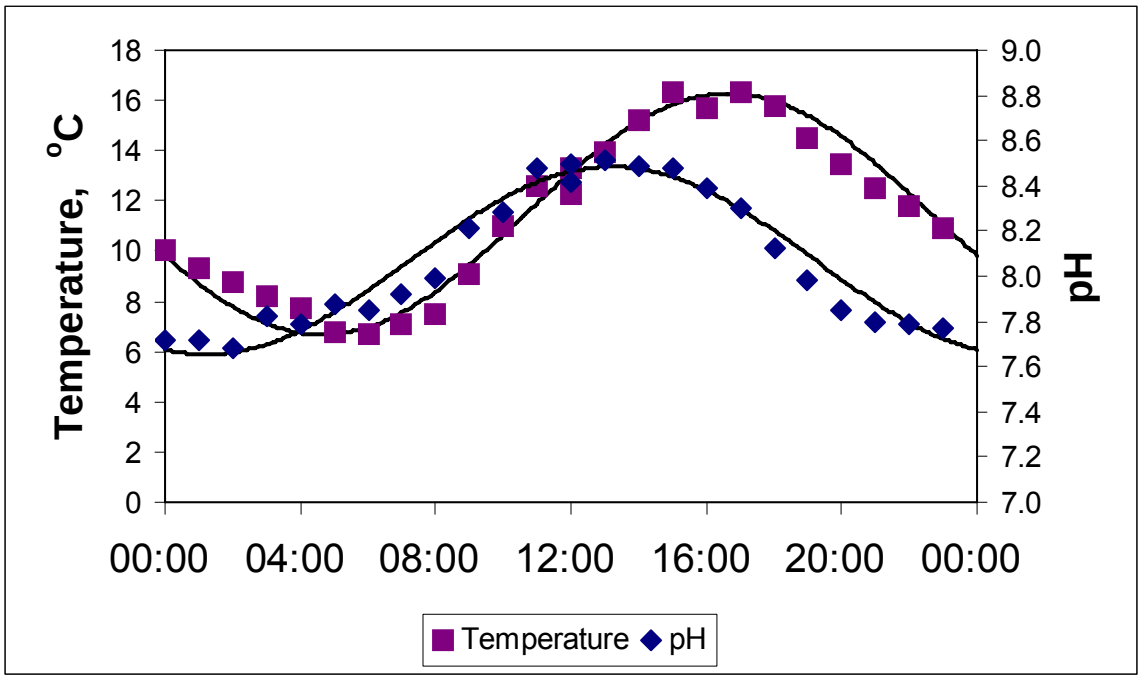

Figure 6. Diel patterns of pH and temperature in Boulder Creek, with sine curves fitted to the observations.

Seasonal variation in pH does not exhibit as strong a pattern as that observed for temperature (Figure 7). Daily minima appear to be relatively stable across seasons, but the maxima tend to be higher in the summer months. Seasonal changes in amplitude are therefore driven by changes in the daily maximum rather than the daily minimum.

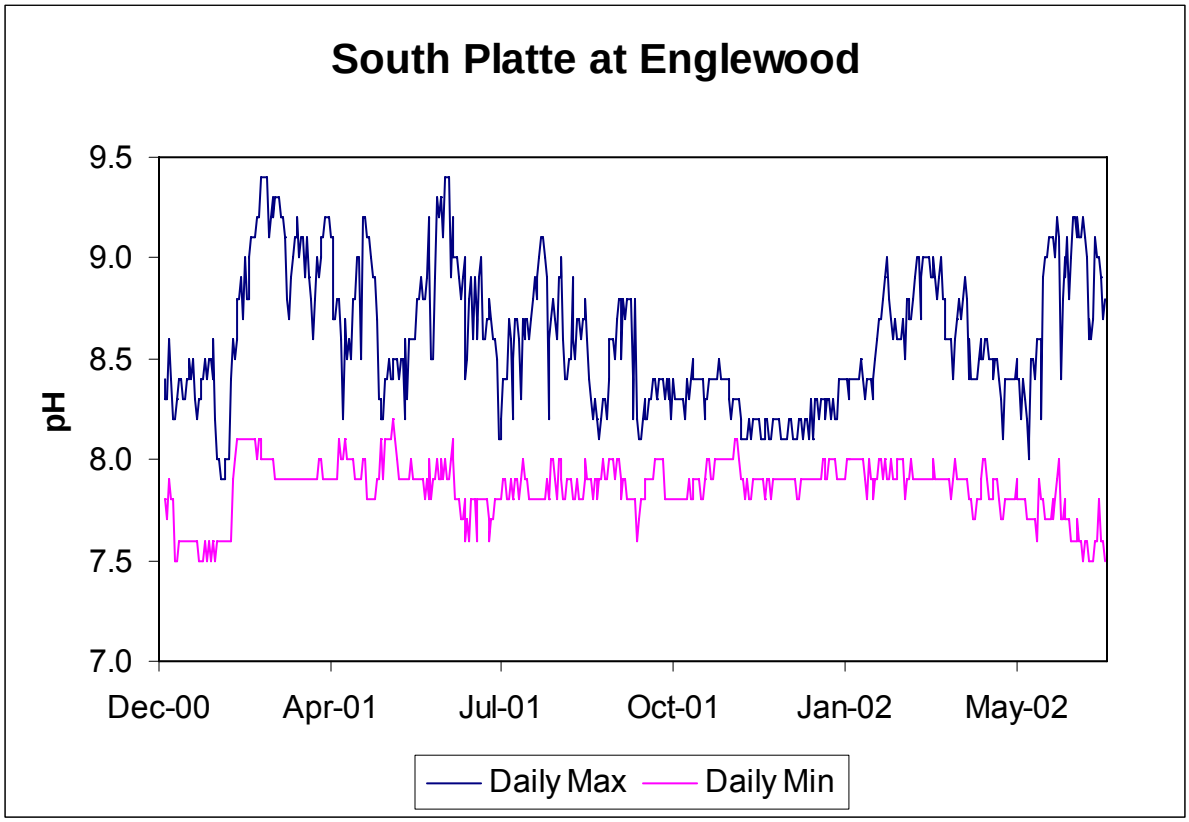

Figure 7. Daily variation in maximum and minimum pH recorded in the South Platte River at Englewood.

Given the pattern of diel variation in both pH and temperature, grab samples taken randomly with respect to time of day are likely to be poor representations of daily mean values. Because the 24-h patterns of variation are predictable for both temperature and pH, however, they provide a good mechanism for using grab sample values to estimate daily mean values based on the time of collection (Figure 8):

$$\overline{T} = T_0 - A * \sin[2\pi * \frac{t_0 - (t_{\max} - 6)}{24}]$$

where $\overline{T}$ = daily mean temperature
T_o = grab sample temperature
t_o = sampling time
t_{max} = time of the maximum
time offset = t_o - (t_{max} - 6)
A = amplitude of diel variation

Once the daily mean has been determined using grab sample data, the equation can be rearranged for predicting values at any time of the day.

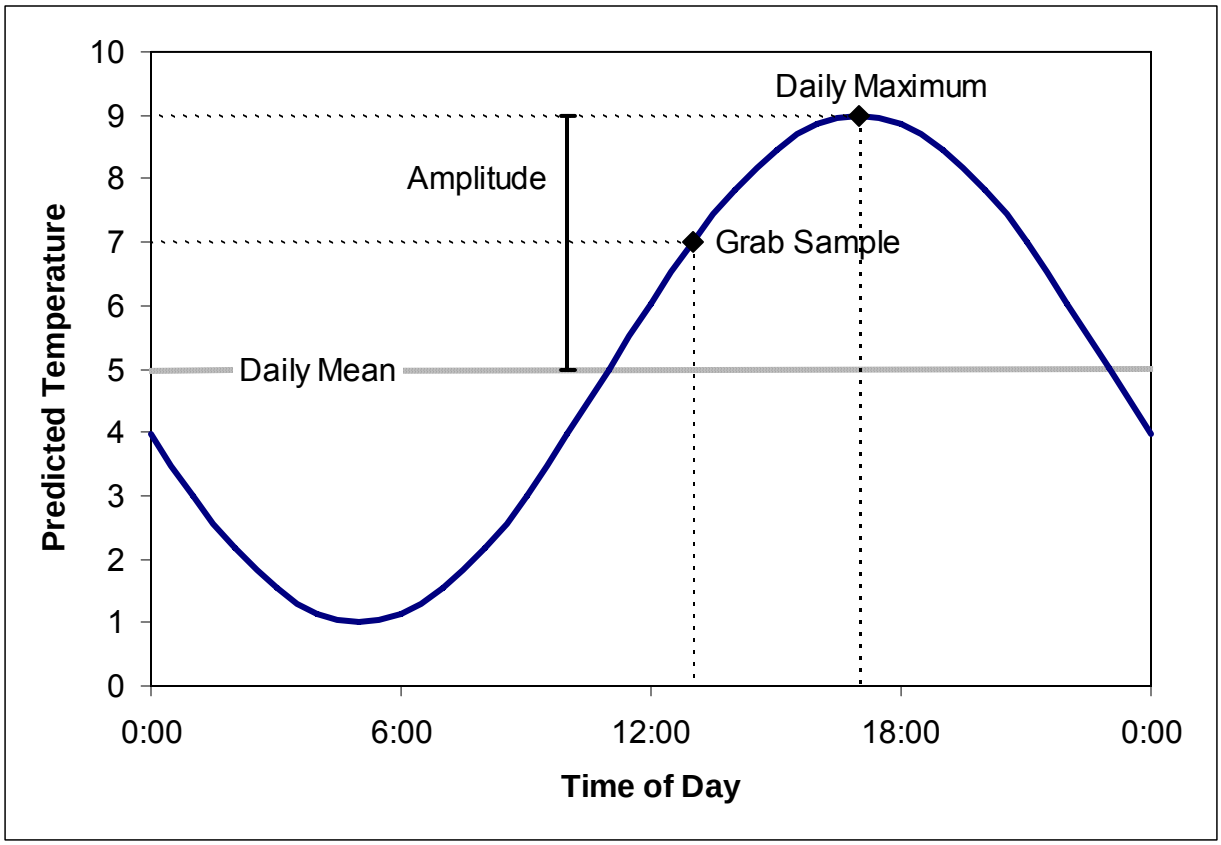

Figure 8. Daily pattern of temperature predicted with a sine function positioned by means of a single grab sample measurement. The amplitude (one-half of the daily range) was set to 4°C and the time of the maximum was set at 17:00. See text for complete explanation of the equations used.

The existence of pattern in the variation of pH and temperature focuses attention on the importance of the timing and scope of field data collection required for supporting calculation of standards. The frequency of data collection determines the extent to which temporal variation can be resolved. Typical frequency of collection for routine water quality monitoring, which might be on the scale of daily to monthly, can provide seasonal, but not 24-h, characteristics of variation. If significant variation occurs on a time scale shorter than the sampling interval, such patterns must be defined even if they are not measured routinely. In the case of pH and temperature, diel (24-h) variation typically is significant.

In order to capture properly the patterns of temporal variation, the ideal data set would consist of a multi-year, hourly record of pH and temperature from which numeric standards could be computed for successive averaging periods. Few water quality data sets are ideal in this sense, and it is rarely practical to contemplate collecting such a data set. Most monitoring programs consist of weekly or monthly grab samples. Therefore, estimation procedures must use the existing data as a framework for constructing the probable characteristics of the ideal data set.

Characterization of temporal patterns of variation in pH and temperature (either measured in the field or estimated from default conditions set in AMMTOX) provides the link between field conditions and regulatory concept. A modest investment of effort independent of routine monitoring can support the creation of a set of equations describing diel patterns of variation for pH and temperature. These equations predict hourly values of pH and temperature on each sampling date during the period of record.

The capacity to define stream standards on a temporal scale that reflects daily patterns of toxicity is a precursor to setting permit limits, as will be discussed in subsequent sections. A central task of the modeling effort is the application of a recurrence analysis, using a once-in-three-year frequency threshold, for defining the toxicity conditions in the stream that will serve as a basis for setting permit limits. The recurrence analysis is based on toxicity, but also must yield the set of environmental conditions associated with it (i.e., pH and temperature for the chronic standard).

Application to Acute Conditions

Acute toxicity of ammonia is determined by stream pH, and the acute standard is based on the highest hourly average pH on any day. Because stream pH exhibits a clear, diel pattern of variation, the time of sample collection must be chosen carefully, or the measured value must be adjusted to account for the known pattern of variation. When it is not possible to measure the maximum pH on every day of a routine monitoring program, the daily maximum must be calculated using the procedure described previously.

If the CMC is based on a grab sample taken at a time of day other than when the maximum pH occurs, and no adjustment is made to account for the diel amplitude of pH variation, the error in calculating the standard can be large. For perspective, a comparison is made between a standard calculated with a grab sample pH and a standard calculated from the maximum pH of the day. If we assume that grab samples are taken typically during daylight hours, a reasonable pH would be greater than or equal to the mean from the sine function. Thus, a comparison of the mean and the maximum is a reasonable assessment of potential error; the error could be larger, however, if the grab sample were taken at night.

The magnitude of the potential error depends on the amplitude of pH variation and the magnitude of the grab sample value. In absolute terms, the potential for error is greatest at lower pH and at high amplitude of pH variation. In a relative sense, however, error is greatest for mid-range pH and high amplitude of variation (Figure 9). When pH is in the range of 7.5 to 8.0, a very common range for streams, and amplitude is in the range of 0.5 to 1 pH units, the CMC may be overestimated by a factor of 2 to 6. Clearly, failure to account for diel variation in pH can impose a significant risk that protection of aquatic organisms will not be adequate.

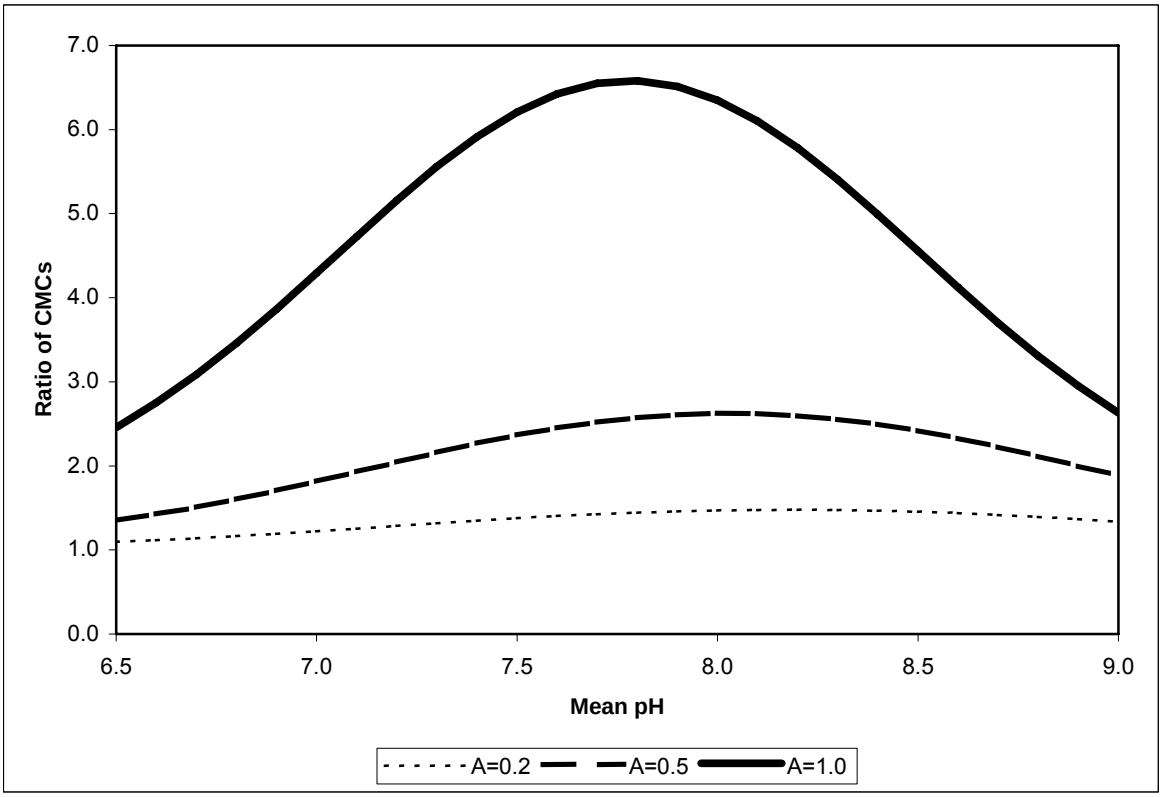

Figure 9. Ratio of CMC calculated with daily mean pH to that calculated with daily maximum pH, as a function of mean pH. Curves are calculated for three different amplitudes (A) of pH variation.

AMMTOX estimates the average pH on each day that a grab sample was collected. The maximum will be calculated after the interpolation step. Unless pH is available on every date in the period of record, some interpolation is required before assessing the probability of exceedances. Linear interpolation is used to set values for days between sampling dates. The end result is a time line with a daily step on which the average pH appears for each day in the period of record. Estimation of values by linear interpolation between sampling dates involves some error. However, experience with existing data records indicates that the amount of error inherent in this type of interpolation is relatively small, and is offset by the benefits of a quantitative system for setting the allowable total ammonia in the stream in conformance with the recurrence interval and averaging period requirements of the numeric standard. After the interpolated data set has been prepared, the maximum is calculated on each day by adding the month-specific amplitude to each daily average pH.

The procedure for estimating the exceedance threshold is based on maximum pH. The number of exceedances (N) consistent with a 3-y recurrence interval is calculated by dividing the total number of days in the period of record by 1095 (= 3y * 365d/y) and rounding to the nearest integer. The $(N+1)^{th}$ highest value from the set of maximum pH values determines the limiting condition for the stream (i.e., the acute standard). For example, if the period of record is 1000 days, one exceedance is allowed (N=1) and the second highest pH becomes the limiting condition. The value derived from the entire period of record, will be more extreme than any measured values in most months. Derivation of limiting total ammonia concentrations requires a ranking of all pH values for each month over the entire period of record. The most extreme value in each month represents a zero exceedance condition. The threshold values for

each month will be set equal to the zero exceedance condition for the month, or the threshold pH, whichever is less restrictive.

Because the model deals with extreme pH values for determining instream conditions, the potential exists for pH to exceed the maximum (9.0) specified in the National Criteria document. It is not uncommon, however, for the daily maximum pH to be in excess of 9 in many streams. Given the practical need for dealing with such a situation, the model will provide a calculation of the standard, but with acknowledgement that it is outside of the range for which official values have been defined.

Application to Chronic Conditions

Chronic toxicity of ammonia is determined by stream pH and temperature. The chronic standard applies to an averaging period of 30 days. Diel and seasonal patterns of variation in pH and temperature create a pattern of variation in toxicity that must be recognized when defining the toxicity conditions that match the recurrence objective. At the same time, the modeling procedure must permit convenient extraction of the environmental conditions associated with the recurrence threshold for toxicity. Ultimately, the pH and temperature associated with the toxicity threshold in each month must be available for mass balance modeling, which is described in a later section.

Temperature and pH typically show diel variation in a pattern that can be described with a sine function, as discussed previously. Calculation of the temperature-dependent component of the CCC, using a sine function to produce temperatures for each hour on the day, shows the effect of the nonlinear function (Figure 10). The shape of the function is not symmetrical, and the average of the hourly values is larger than the value of the function evaluated for mean daily temperature. The effect of diel variation in pH is even more pronounced with respect to the shape of the function and the bias that would be introduced if the pH-dependent component of the CCC were calculated from daily mean pH (Figure 11).

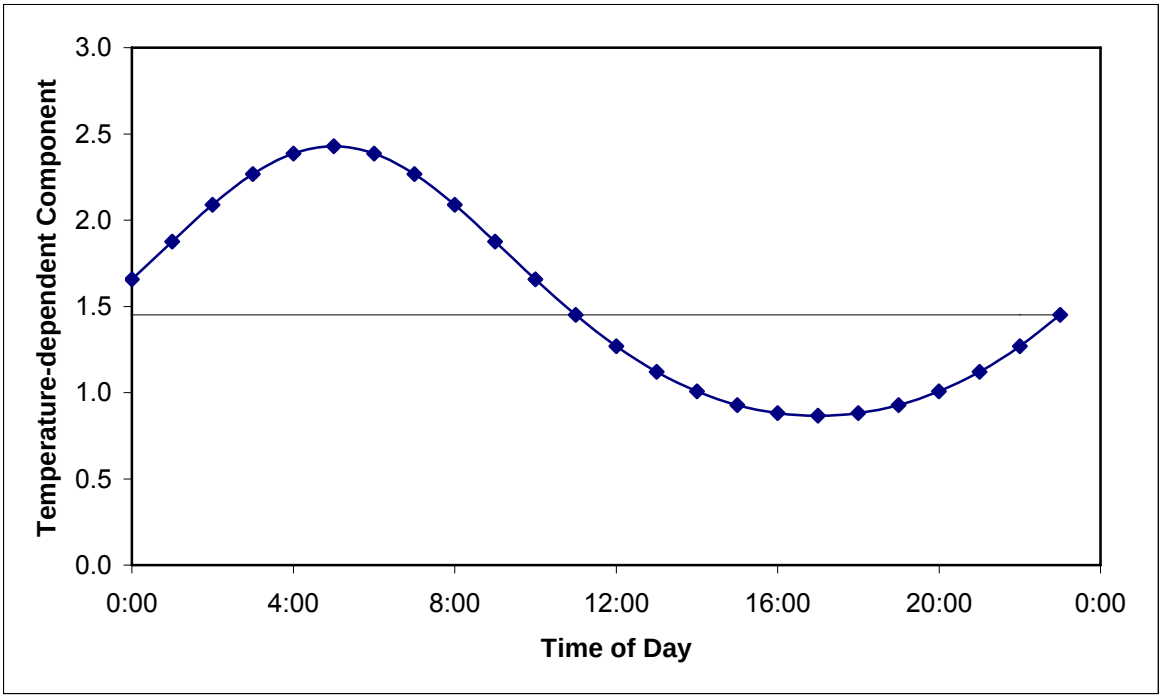

Figure 10. Hourly values for the temperature-dependent component of the CCC with mean temperature at 25°C and amplitude at 8°C. The solid horizontal line shows the value of the function evaluated at 25°C.

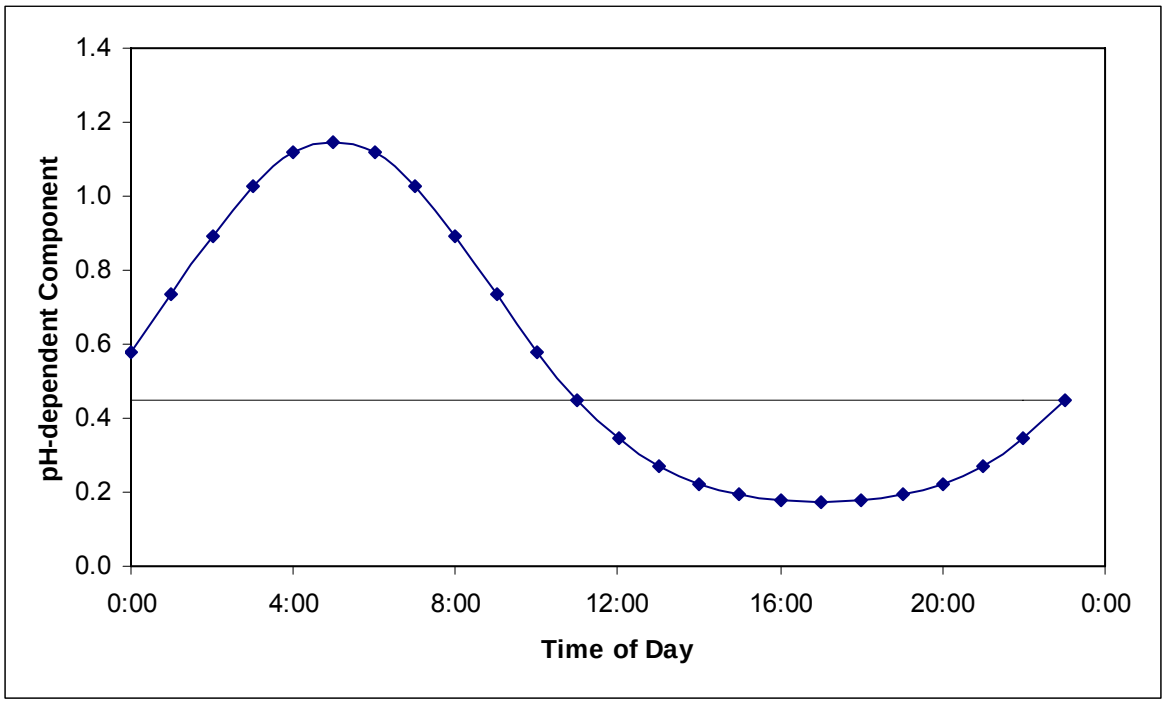

Figure 11. Hourly values of the pH-dependent component of the CCC with mean pH at 8.5 and amplitude at 0.6. The solid horizontal line shows the value of the function evaluated at pH=8.5.

Increasing the amplitude of temperature variation shifts the daily mean of the temperature-dependent term away from the value calculated for a constant temperature equal to the mean. The general pattern shows that the amount of the shift (i.e., bias) increases with increasing amplitude (Figure 12). The 10°C line is truncated at an amplitude of 3°C because the comparison would have been distorted by influence from the temperature cap at 7°C. Bias in the temperature component varies linearly with the square of amplitude, but is independent of the mean, provided that the minimum daily temperature is not less than the cutoff (7°C for the CCC).

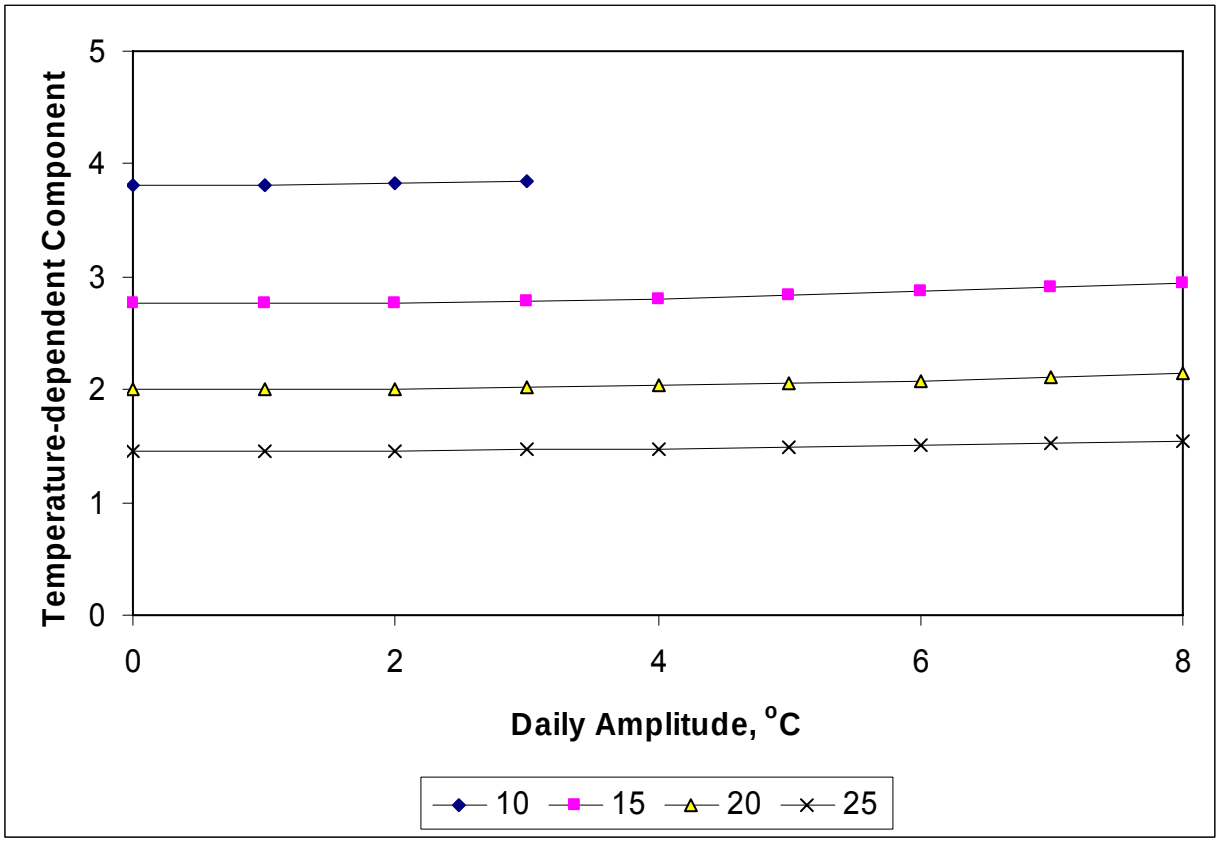

Figure 12. Effect of diel temperature variation on calculation of the temperature-dependent component of the CCC. The four lines represent daily mean temperatures of 10, 15, 20, and 25 °C. The value shown for amplitude of zero represents the standard that would be calculated using mean daily temperature.

A similar investigation of the pH-dependent component shows that the divergence of the average of hourly values from the value based on average daily pH increases as the amplitude of variation increases (Figure 13). At high pH (e.g., 8.5) and high amplitude (e.g., 0.6), calculation of the pH-dependent term from the daily average pH will underestimate the true value (based on average of hourly terms) by about 20%. Amplitude has no effect when mean daily pH matches the transition pH (7.688) in the formula for the CCC.

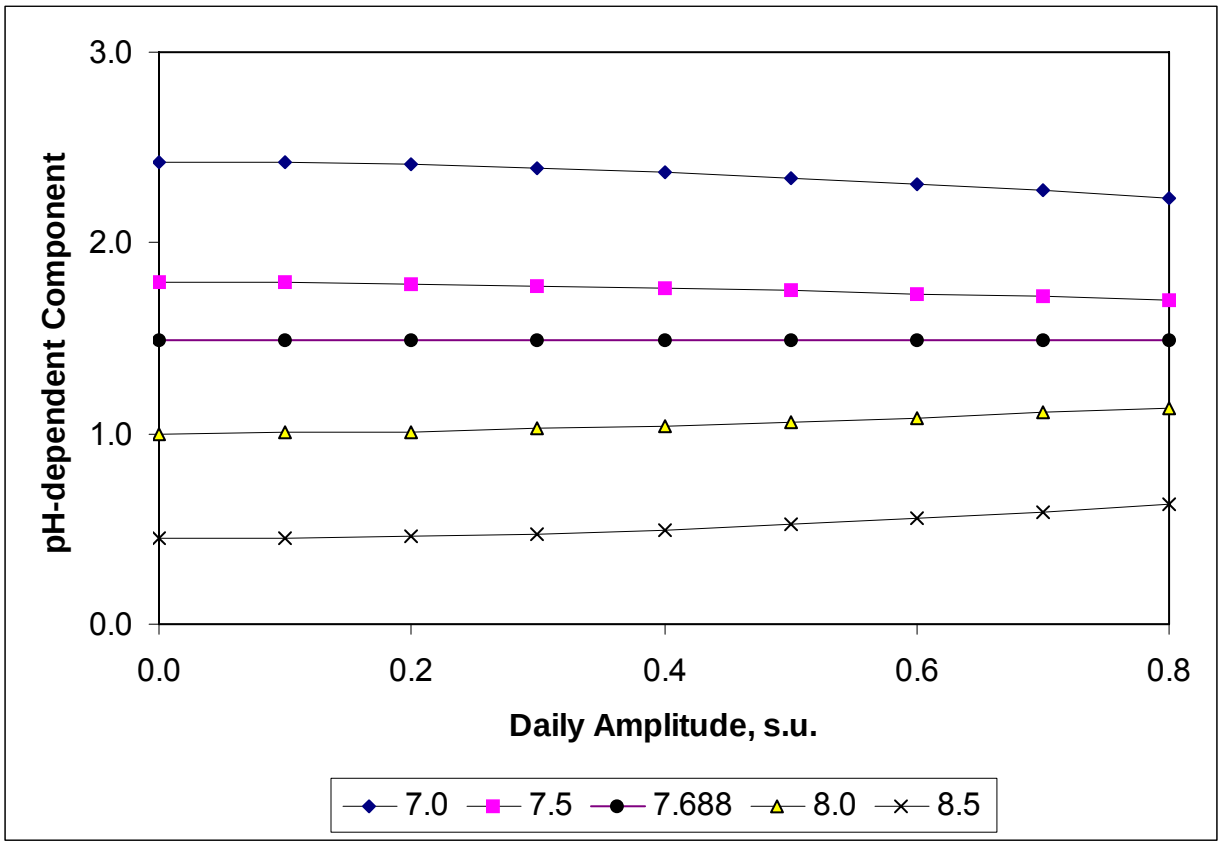

Figure 13. Effect of diel pH variation on calculation of the pH-dependent component of the CCC. Four plotted lines represent daily mean pH of 7.0, 7.5, 8.0, and 8.5. Amplitude has no effect if the daily mean matches the transition pH of 7.688. The value shown for amplitude of zero represents the standard that would be calculated using mean daily pH.

The CCC is calculated using the product of the pH- and temperature-dependent components. Bias in the daily average value for the CCC is influenced by contributions of bias from both component terms. Calculation of the CCC with daily average pH and temperature introduces a very large bias in the CCC, to the extent that it may be 30-40% lower than the average of hourly CCCs when the amplitudes of variation are high for both pH and temperature. The bias can be reduced substantially, for any reasonable set of values, by calculating the daily average from 4 points (maximum, mean, minimum, mean) that can be constructed efficiently from the interpolated mean and the amplitude applied in each month. There is essentially no bias when the 4-point mean is used with data sets where the mean temperature is at least 15°C; at lower temperatures, the bias does not appear to exceed 1%.

Determining the appropriate threshold value consistent with the once-in-3-year recurrence objective is more complex for the chronic standard than it is for the acute standard. However, an appropriate concept can be derived from EPA's biologically-based, low-flow procedure, which provides a method for estimating the number of excursion days above a specified threshold for an uninterrupted sequence of daily measurements. The procedure is iterative, and could logically begin with the second highest value drawn from the complete set of 30-d averages. Each day in the period of record is scored with respect to the threshold value as follows: if the date in question is part of any 30-d average that is greater than the threshold, it is scored as an excursion. If not, it is ignored. The total number of excursions divided by 30

is the number of exceedances. The threshold is increased or decreased iteratively until the number of exceedances is as close as possible to 0.33 per year. The threshold establishes the worst-case condition for regulatory purposes. When limits are set for each of the 12 months, the appropriate value will be the largest observed value for the 30-d averages in that month (across all years), or the threshold, whichever is smaller.

The chronic threshold is based on a standard from which it is not possible to extract the unique pairings of pH and temperature that define setpoint conditions in each month. The difficulty is due in large part to the formulation of the temperature dependent component, for which the value reaches a plateau below 7°C when ELS are absent, or below 14.4^{o}C when ELS are present. To circumvent this problem, a simplifying assumption is required. In AMMTOX, setpoint temperature for each month will be defined as the median of the daily mean temperatures in the interpolated data set. Application of this assumption will yield a reasonable value for adjusting the ammonia removal rate, and a typical, but not extreme, value for the temperature component. The tradeoff makes sense for practical reasons, and will not undermine protection of aquatic organisms as will be explained next.

Procedures employed to this point have produced a value for the chronic standard in each month, and a typical temperature from which the temperature component of the standard can be calculated. Given the CCC and the temperature component in each month, the pH component can be obtained by simple division, and the associated pH can be found in a lookup table. The pH component determined by this procedure will be consistent computationally with the CCC and the temperature component. If the pH component were derived by the threshold procedure, the product of the temperature and pH components probably would not match the CCC determined by the threshold procedure. Thus, the procedure devised for AMMTOX will extract stream pH and temperature values consistent with the limiting condition for the CCC, and these pH and temperature values will provide a crucial input to the mass balance model.

Mass Balance Modeling: Creating the Link Between Effluent Limits and Stream Standards

AMMTOX establishes the link between instream standards and permit limits by modeling the processes that define the controlling conditions for ammonia toxicity and predict the biological removal of ammonia. Simple mass balance calculations describe conditions at the point of mixing, but four processes occurring simultaneously and rapidly will alter initial conditions as water moves downstream from the outfall: (1) biological conversion (e.g., algal uptake and nitrification), which reduces the amount of total ammonia, (2) pH rebound, which causes the pH of the mixture to rise to an equilibrium value (pH setpoint), (3) temperature rebound, whereby the mixture warms or cools to come into equilibrium with the stream conditions (temperature setpoint), and (4) addition of assimilative capacity through tributary inflows and net accrual of groundwater seepage.

Modeling Concept

An instream standard establishes a threshold above which the concentration of a constituent may harm aquatic life, or impair other designated uses. In most streams, some assimilative capacity exists because natural concentrations are less than the standard. The assimilative capacity can be allocated to one or more dischargers by setting limits on the concentration of each constituent in the effluent.

Ammonia presents a formidable challenge because it is non-conservative (i.e., concentrations are affected by biological processes), and because toxicity is affected by environmental conditions (pH and temperature) that can change significantly, particularly in "effluent-dominated" streams, as the water mass travels downstream from the mixing zone (Figure 14). The typical pattern of change in environmental conditions causes toxicity to increase with distance from the outfall. At the same time that the toxicity is increasing, the concentration of ammonia may decline through biological conversion. The net effect of increasing toxicity and decreasing concentration is often a downstream displacement of the conditions that will control the permit limit (Figure 15).

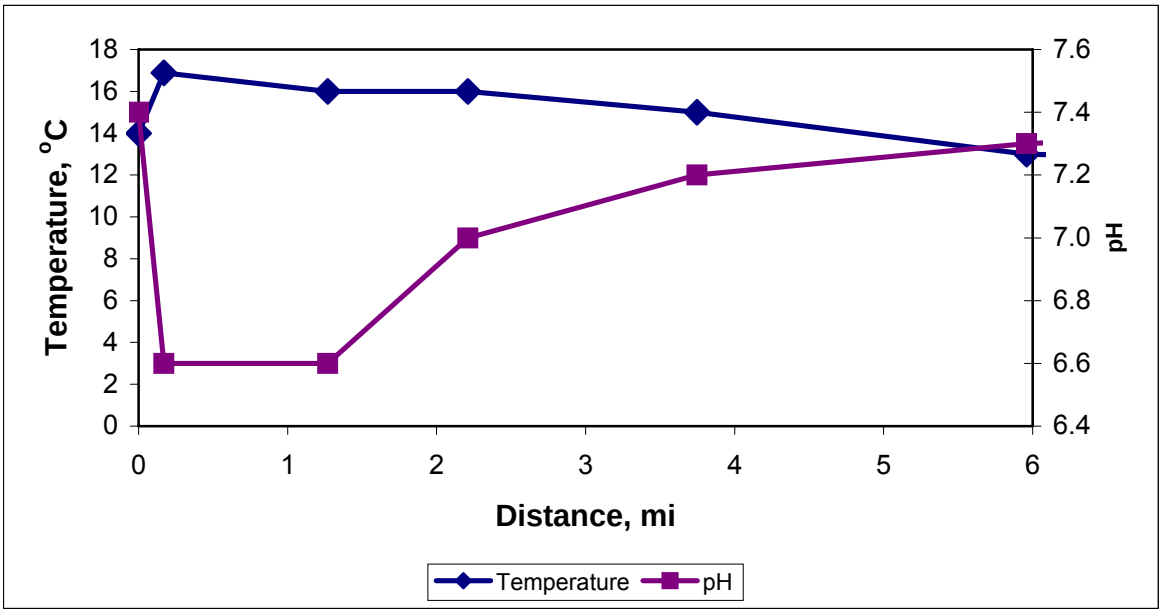

Figure 14. Longitudinal profiles of temperature and pH in the South Platte River showing the influence of a large wastewater discharge. The large depression of pH is transitory, as discussed in the text.

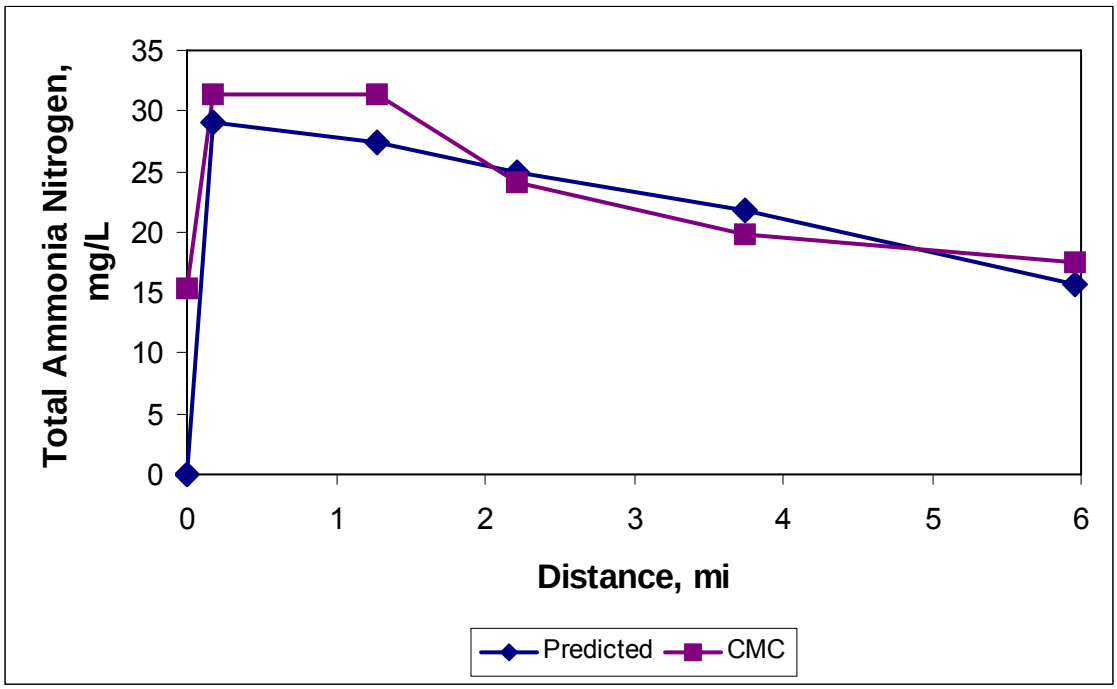

Figure 15. Longitudinal profiles of total ammonia for the scenario described in Figure 14. The concentration predicted in the stream is based on hypothetical removal rates. The CMC is based on the pH and temperature values shown in Figure 14. A lower CMC indicates higher toxicity. The point at which the predicted concentration exceeds the CMC (at about 2.5 miles) represents the controlling condition.

Downstream displacement of the controlling conditions means that assimilative capacity can be higher than would be predicted on the basis of mixed conditions just below the outfall. Assimilative capacity increases because ammonia decreases between the outfall and the controlling point (Figure 15). In essence, this is a credit that should accrue to the discharger; otherwise, permit limits will be more stringent than is necessary to protect designated uses.

The mass-balance component of AMMTOX consists of a series of short stream reaches within which the mass of ammonia is altered through changes in flow (tributaries, diversions, or seepage), or by biological processes occurring within each reach. The amount of processing that can occur within any reach depends on temperature and time of travel. Ammonia remaining at the downstream end of one reach provides input to the next reach (Figure 16).

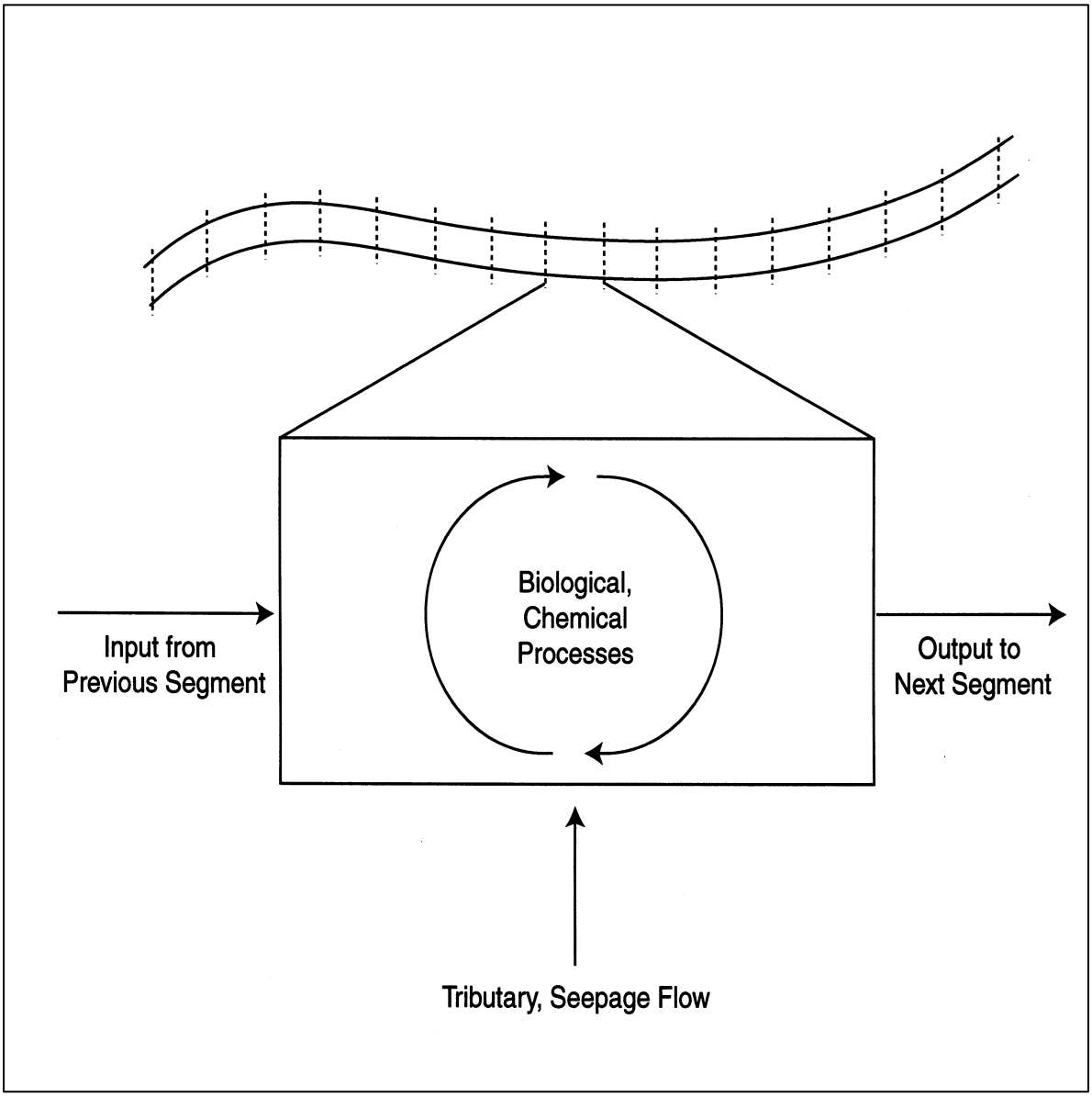

Figure 16. Conceptual representation of structure and processing in AMMTOX.

Defining Hydrologic Conditions

Operation of the mass balance model requires an accurate rendering of hydrology as a pre-requisite for calculating mass transport and for determining stream velocity. Low flows above an outfall are defined according to the relevant regulatory requirements. Biologically-based low flows (30-day, 3-year chronic flow and 1-day, 3-year acute flow) are preferred for this analysis but other measures of low flow such as ${}_7Q_{10}$ can be used instead. Biologically based low flows can be determined with EPA's DFLOW program (Rossman 1990). Low flow analysis is the responsibility of the user; AMMTOX does not perform any low flow analyses.

If the hydrologic scenario is more complex, with several dischargers or tributaries, and some diversions, specification of flows becomes much more challenging. Low flow analysis could be applied separately to each tributary, but this procedure will tend to underestimate the true combined flow unless there is a high degree of coincidence in the extreme low flows of the main stem and its tributaries. Low flow analysis also is not well suited for estimating the role of withdrawals, which tend to be high when water is available and may be low when constrained by available flow or water rights considerations.

One strategy for defining low flow conditions is based on preservation of a low flow regime along the main stem. Daily flows at selected locations along the main stem are calculated from gage records and daily flows for additions and withdrawals. A low flow analysis is performed for the main stem above and below each addition (or withdrawal). The change in flow required to maintain the historical low flow regime of the main stem is determined by difference. For example, if the biologically-based low flow above a tributary is 33 cfs and the comparable value below the tributary is 38 cfs, the tributary must contribute 5 cfs, in the context of modeling, to maintain low flow conditions in the main stem.

Effluent contributions are set to design capacity, as is required for permit analysis. If the modeling scenario involves several dischargers, the main stem will register flows in excess of historical flows by an amount roughly equal to the difference between historical effluent flows and design capacity. This may be realistic in some situations, but may not make sense in a highly managed system.

Defining Water Quality

Water quality characteristics of headwaters and tributaries are established using median values in each month for temperature, pH, and total ammonia. Temperature and pH should be adjusted to daily average values before medians are calculated. Medians are preferred unless there is a strong correlation between flow and these constituents. Effluent is added at design capacity flow and with median pH and temperature. Temperature and pH of the effluent may be set according to expected values if there is no historical record of operating conditions. Effluent ammonia concentration will be adjusted by iteration until the limit is determined.

At the point of discharge, volume-weighted means of effluent and stream values are calculated for temperature and total ammonia. The best estimate of mixed pH, in the absence of a direct measurement, is the volume-weighted mean hydrogen ion concentration. This approach is quite satisfactory for most situations, but users should be cautious if the alkalinity of the effluent differs greatly from that in the stream (cf. Jordan 1989).

Setpoint and Rebound

After mixing effluent with the receiving water, the model must predict changes in pH and temperature as the water mass travel downstream. The spatial pattern of pH and temperature will determine the spatial pattern of ammonia toxicity, and changes in temperature will affect the biological processing of ammonia. Simplifying assumptions are used to make the predictions tractable for pH and temperature because a formal, mechanistic approach to modeling either is rarely feasible. Incorporation of an empirical

characterization of pH and temperature rebound provides a simple, realistic picture of stream chemistry below an outfall.

The first assumption is that, on any given day, there is an “equilibrium” value for the pH and temperature of the mix of effluent and stream water. It is an equilibrium value in the sense that the depression of pH and alteration of temperature, caused by addition of effluent to the stream, are transitory; conditions in the stream will return to “normal” after being perturbed by the effluent discharge. From the set of equilibrium values, a limiting condition, called the “setpoint,” is determined by recurrence analysis. The setpoint represents an extreme condition (once-in-three year recurrence) for the environmental conditions affecting ammonia toxicity, and it constitutes a target governing the downstream trajectory of pH or temperature. Separate setpoints are determined for the chronic and acute conditions in each month.

For acute conditions, where toxicity is a function of pH alone, setpoint is simply the maximum pH in every month, not to exceed the once-in-three-year threshold value. Because the acute standard does not incorporate temperature, but temperature is still needed for predicting biological removal of ammonia, the acute setpoint temperature will be set equal to the chronic setpoint temperature.

The concept is more complex for chronic conditions, where toxicity depends on two variables and the averaging period is long relative to typical patterns of variability. In this case, setpoint represents the pH and temperature conditions associated with the chronic standard, not to exceed the once-in-three-year threshold value. For chronic conditions, setpoint is not simply a recurrence analysis of pH or temperature, but rather of the standard, from which the associated environmental conditions are reconstructed. Viewed another way, it is a set of pH and temperature values that allow one to obtain the relevant standard. The values of pH and temperature are needed to calculate standards at any point below the outfall. Temperature also guides changes in the ammonia removal rate.

The second assumption is that downstream trajectories for pH and temperature are linear, with constant rebound rates that depend on distance. Rebound rates determine how far the mixture travels before setpoint conditions are achieved. The distance (or time) required for the pH or temperature of the mix to reach setpoint is determined by the rebound rate. The model relies on a linear rate of change over distance for pH and temperature. Default rates are 0.2 units/mi for pH and 0.7^{o}C/mi for temperature.

Implicit in the setpoint procedure implemented in AMMTOX is the assumption that extreme values of ammonia toxicity (i.e., setpoint) are likely to coincide with low flows of regulatory interest. Obviously, this is a conservative position, and one that may not be realistic. In a study of 12 sites in Colorado, Lewis and Saunders (1995) found only one site at which the values of pH and temperature (presented in the paper as the fraction un-ionized because stream standards in Colorado are for un-ionized ammonia) during extreme low flows were significantly higher than the values of pH and temperature at other flows. When the association between low flows and pH/temperature conditions is weak or absent, the recurrence interval for the controlling conditions will be lengthened, perhaps significantly. A protocol for evaluating the appropriateness of this very conservative assumption is described in Lewis and Saunders (1995).

Processing in the Stream

The concentration of total ammonia decreases downstream through biological processes. Removal of ammonia is simulated with first-order kinetics, as is common in most stream models. Use of first-order kinetics does not imply knowledge of the primary locus for ammonia removal, e.g., benthos or plankton (Cooper 1984, 1986), or the dominant biological mechanism. Nitrification is the chief process responsible for the removal of ammonia in most streams. Where suitable conditions exist, uptake by benthic algae also may be important for removing ammonia from the stream. Because nitrification probably is not the only process regulating ammonia concentration, the process should be regarded as aggregate removal rather than simply nitrification.

Ammonia loss rates vary widely among sites throughout the U.S. (Table 7). The Colorado Department of Public Health and Environment (CDPHE), recognizing the tendency of Colorado streams to show high ammonia loss rates, uses a default rate of 6.0 d^{-1} (base e, adjusted to 20°C) in the Colorado Ammonia Model for developing permit limits. The same default rate will be applied in AMMTOX. A temperature compensation factor (Θ) of 1.08 is used in the model such that $K(T) = K(20)\Theta^{(T-20)}$ (Bowie et al. 1985; Zander and Love 1990). Site-specific studies are recommended, but require some experience to design correctly. Results may be sensitive to cloud cover if algae play a major role in ammonia removal.

Stream	Removal Rate, d^{-1}	Source
Arkansas River below Pueblo	10.7	Lewis and Saunders, unpublished
Boulder Creek below Boulder	7.8	Lewis and Saunders, unpublished
Cache la Poudre above Ft Collins	7.3	Lewis and Saunders, unpublished
Cache la Poudre below Ft Collins	12.8	Lewis and Saunders, unpublished
Cache la Poudre near Windsor	5.0	Lewis and Saunders, unpublished
Coal Creek below Lafayette	4-11	Lewis and Saunders, unpublished
Fountain Creek	3.2-15.2	CDPHE
Marcy Gulch	1.5-9.5	CDPHE
Monument Creek	13.0	CDPHE
South Platte in Denver	9.5	Lewis and Saunders, unpublished
South Platte in Denver	0.5-1.0	Paschal and Mueller 1991
Yampa River	7.9	CDPHE
14 sites, U.S. and New Zealand	0.2-7.2	Cooper 1986
8 studies, U.S.	0-9.0	Bowie et al. 1985

Table 7. Ammonia loss rates, adjusted to 20°C, for selected streams chiefly in Colorado. Most rates were determined by the Center for Limnology in support of analyses recommending permit limits.

Ammonia concentrations also can decrease when flow is added downstream of the effluent outfall. Some streams receive substantial additions of water from seepage, which can be defined broadly to incorporate surface runoff, groundwater accrual, agricultural returns, and small, ungaged tributaries. This is especially true where there is extensive irrigation in a watershed. Addition of seepage increases the assimilative capacity of the stream because groundwater rarely contains significant amounts of ammonia. Therefore, inclusion of seepage can increase effluent limits for total ammonia in cases where the controlling condition is downstream of the outfall. In contrast, the loss of stream flow to the alluvium has a relatively insignificant impact on discharge limits because ammonia concentrations in the stream are not altered.

Stream Velocity

At a given temperature, the amount of ammonia that biological processes can remove from a given stream reach depends on the time of travel, which is calculated from reach length and stream velocity. There are a number of ways that velocity can be characterized for the model depending on the information available to the user. One approach involves hydraulic geometry equations, in which a power function describes velocity (V) as a function of discharge (Q; see below). The constant (k) and exponent (m) of this equation are entered on the control page of the model. If the equation is not available from previous studies, it may be derived from information available to the user. The USGS, or a cooperating agency, collects the necessary information when establishing a rating curve at a gaging station. Access to, and use of, this information is described in Leopold (1997). For many gaging stations, the field measurements supporting the rating curve are available on the USGS NWISWeb Data site under “surface water: measurements.” Jowett (1998) describes a simplified procedure for estimating the equation

based on measurements of discharge and channel cross section at two different flows. The exponent of the hydraulic geometry equation can often be estimated based on properties of the stream channel. Rhodes (1977) provides a classification system that can help in the selection of the exponent. A selection of values reported in the literature is shown in Appendix B. The exponent is not sufficient alone, however; one would also need measurements of discharge to calculate the coefficient for the equation.

$$V = kQ^m$$

Velocity can also be estimated from Manning's equation (see Gordon et al. 1996), which requires information on roughness, channel slope, and hydraulic radius. Roughness can be estimated from standard tables, channel slope can be estimated from field surveys or topographic maps, and hydraulic radius can be calculated on the basis of channel shape. Hydraulic radius is the ratio of cross sectional area to wetted perimeter. Calculation of the hydraulic radius, R, can be simplified somewhat by assuming that the channel section matches a standard geometric form (e.g., rectangle, trapezoid, parabola, etc; see Chow 1959 Table 2-1). When stream width is much greater than depth, R is approximately equal to the average depth (Hornberger et al. 1998). Many sources exist for the roughness (Manning's coefficient, n)(e.g., Chow 1959). The advantage of Manning's equation over field measurements of velocity is that the result would be applicable to a reach rather than a point or cross section.

$$V = (1.486/n)R^{2/3}S^{1/2}$$

V = velocity, ft/s [For metric units, the factor 1.486 becomes 1.0.]
R = hydraulic radius
S = slope
n = Manning's coefficient

Perhaps a simpler approach, if field measurements are required, is to estimate velocity under low flow conditions. Measurement devices can be as simple as a float (oranges work very well because the density is only slightly less than that of water) or much more complex if flow-measuring devices are available. The disadvantage for this approach is that velocity for the low flow condition of regulatory interest may be substantially lower than velocity under the measured conditions.

When velocity is not determined by channel geometry, individual values must be entered in the appropriate cell for each reach. Field measurements at low flow would give a reasonable estimate of velocity for modeling, but may require considerable effort to obtain broad geographical representation.

Stream Monitoring Data

The data required for AMMTOX include a routine component that will be subject to the recurrence analysis, and a non-routine component that targets patterns of variation and removal processes.

Routine Monitoring Data

AMMTOX is designed to operate with grab sample data that should be available from most routine monitoring programs. Collection sites for routine grab samples should be selected with care. Ideally, grab samples should be taken far enough below an outfall to be clear of rebound processes, but still within a region where the stream and one effluent are the dominant influences. Data from this site will be used to characterize setpoint conditions, and thus represent an endpoint for changes in pH and temperature that are the result of mixing effluent with stream water. In most cases, rebound is complete within a few miles of the discharge point. Alternatively, it may be suitable to sample the stream above the outfall.

Where there are multiple dischargers or significant tributary contributions, there may be limited flexibility in site selection. Moreover, it may be necessary to use sites where a good data record already exists. In view of these common constraints, it is helpful to bear in mind that the broad objective is one of characterizing downstream trends in temperature and pH. In a complex urban setting where no single, ideal location exists for establishing setpoints, data from several sites can be analyzed. Although full rebound may not be achieved at any one of these sites, the set of sites should define the longitudinal changes expected for pH and temperature. The present version of AMMTOX allows for use of setpoint data from as many as 6 locations. When more than one setpoint location is specified, each will require analysis with the recurrence module.

Although AMMTOX contains no specific limit on the period of record for grab sample data, six years is probably optimal. Longer or shorter records may be used, but the operator should exercise some judgment when selecting the length of the data record to be analyzed. Stream chemistry is more sensitive to land use changes and to changing effluent loads than it is to stream discharge. The use of very long data records may be especially inappropriate for analyzing pH. Records longer than three years are desirable for statistical reasons; records longer than six years should be scrutinized carefully for trends indicative of secular changes in stream chemistry.

There is no absolute requirement for sampling frequency in AMMTOX, but it is generally expected that monitoring programs for large dischargers will involve weekly or biweekly sampling. The model will function with intervals of any length by performing interpolations to provide values for every day. It is up to the user to decide if analysis of a particular data set is a good idea. **It is strongly recommended that this model not be used where the typical interval between sampling dates exceeds 30 days.**

pH/Temperature Variation

The characteristics of diel variation in pH and temperature must be defined in order to use grab sample data when determining setpoint values. Default values may be selected in the model. If site-specific characteristics of variation will be used, measurements should be made at the same site where grab samples are collected. The model creates 24-h patterns for pH and temperature using grab sample data and supplemental data (default or site-specific). Careful selection of the pH amplitude and the time of the maximum is crucial to model performance, and may require some special sampling. Default conditions can be accepted for the time of the maximum, but there are three default sets for the amplitude of pH variation. Inclusion of some field data creates a more secure basis for selecting the correct set of default amplitudes. These data can be obtained without much difficulty by measuring pH at 1- or 2-hr intervals from sunrise to sunset on a sunny day during the summer. Cloudy days are not desirable because reduced sunlight will diminish photosynthesis, thereby damping the amplitude of pH variation. The sampling probably should be repeated a few times to determine the reliability of the results. Values

obtained from these sampling sets will give an estimate of the daily pH range, which is twice the daily amplitude. The measured amplitude can then be matched to one of the default sets.

Taking enough measurements to create a complete set of site-specific values of amplitudes and times of maximum for pH and temperature variation would require a very data-intensive sampling program that should include 24-h sampling events on a bi-weekly or monthly frequency for at least one year. The amplitude and the daily average value can be estimated by regression analysis using equation (1) if the times of data collection are transformed according to the following equation.

$$h = t_o - (t_{max} - 6)$$

where h = transformed time
t_o = sampling time
t_{max} = time of maximum

The third parameter, t_{max}, in the equation can be set simultaneously with a nonlinear regression technique, or can be varied iteratively and evaluated with linear regression techniques. If the latter approach is taken, the model default time of the maximum provides a good starting point from which t_{max} in the equation can be varied in order to maximize the r^2 of the regression analysis. A certain amount of judgment is required here because a statistical best-fit that places the time of the maximum at midnight makes no sense biologically.

The treatment of temperature variation is very similar to that described for pH, but is simpler because there is only one default set of temperature amplitudes. The suitability of the default amplitude for a specific location can be tested easily as described by Crisp (1990), the gist of which is that a few measurements at fixed times of day will define both the daily mean and the amplitude of temperature variation. The time of the maximum could also be determined by the regression technique described above.

Effluent Conditions

The user must supply the flow, pH, and temperature of each effluent in each month of the year. The design capacity of each wastewater treatment facility is typically used for the flows in each month. In situations where plant design capacity may not be needed until 10 or 20 years in the future, flows can be set equal to the capacity that will apply for the life of the permit. When the lesser flow is used, regulators may stipulate in the permit that the capacity used for modeling cannot be exceeded for the life of the permit. For large wastewater treatment facilities where reliable information exists on seasonal patterns of discharge, it may be possible to specify separate flows for each month of the year, rather than having one value that applies to all months. The potential advantage of this approach lies in matching lower flows with higher total ammonia concentrations on a seasonal basis. There are a variety of approaches that might be taken to determine the characteristic pH and temperature of the effluent in each month. One involves the calculation of unionized fraction in the effluent from all available pH/temperature pairs. The median unionized fraction and the median temperature are determined for each month, and the characteristic pH is calculated by re-arranging the equation for fraction unionized. It is appropriate to focus on typical conditions for effluent because it is unlikely that extreme conditions for the effluent would coincide with those in the stream.

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Appendix A: Equations in AMMTOX and options for changing coefficients

The formulation of the CMC, as shown in equations 13 and 14 of the National Criteria document, represents the culmination of a process in which important decisions are made about component terms, the values of which should be open to change under the appropriate conditions. In the interest of maintaining flexibility in the permitting process, we will take the equations back a few steps making it possible to introduce different values for selected parameters.

We start with equation 7, in which the key parameters pH_T, R, and LIM_L are presented. AMMTOX includes default values for pH_T and R that conform to those presented in the National Criteria document, but either can be changed if sufficient justification exists. Equation 7 can be arranged to define LIM_L in terms of the $LC50_t$, as follows:

$$LC50_t = (LIM_L)\left[\frac{R}{1+10^{pH_T - pH}} + \frac{1}{1+10^{pH - pH_T}}\right]$$

When LIM_L is defined in terms of $LC50_{t,8}$, as appears in equation 8, the second term becomes a constant, which we define simply as B.

$$LIM_L = LC50_{t,8}\left\{\frac{1}{\left[\frac{R}{1+10^{pH_T - 8}} + \frac{1}{1+10^{8 - pH_T}}\right]}\right\}$$

$$B = \frac{1}{\left[\frac{R}{1+10^{pH_T - 8}} + \frac{1}{1+10^{8 - pH_T}}\right]}$$

When default values are used for pH_T and R, the value of B for acute conditions is 6.95, and that for chronic conditions is 2.91. Substitution of B in equation 8 leads to a restatement of equations 11 and 12 such that it is easier to understand the origin of the terms, and to appreciate how each will change when underlying parameters are changed.

$$LC50_t = LC50_{t,8} * B * \left[\frac{R}{1+10^{pH_T - pH}} + \frac{1}{1+10^{pH - pH_T}}\right]$$

$$LC50_t = LC50_{t,8} * \left[\frac{R * B}{1+10^{pH_T - pH}} + \frac{B}{1+10^{pH - pH_T}}\right]$$

Setting $LC50_{t,8}$ equal to $AV_{t,8}$, and substituting acute values for R and pH_T will yield equation 11 (for salmonids present in example shown below); similarly, setting $LC50_{t,8}$ equal to $CV_{t,8}$ and substituting chronic values for R and pH_T will yield equation 12.

$$AV_t = AV_{t,8} * \left[\frac{0.00704 * 6.95}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}} \right]$$

$$AV_t = AV_{t,8} * \left[\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}} \right]$$

$$CV_t = CV_{t,8} * \left[\frac{0.0232 * 2.913}{1+10^{7.688-pH}} + \frac{2.913}{1+10^{pH-7.688}} \right]$$

$$CV_t = CV_{t,8} * \left[\frac{0.0676}{1+10^{7.688-pH}} + \frac{2.913}{1+10^{pH-7.688}} \right]$$

The CCC requires an additional, temperature-dependent term (see equations 19 and 20 in USEPA 1999). Superficially, the form of the equation when ELS are absent appears very different from that when ELS are present. The differences are the result of simplification; a more complex form will show the features common to both equations and make it more transparent when site-specific values are used.

The generalized equation for the temperature-dependent term of the CCC, can be expressed as follows:

$$CCC_{temperature} = 0.854 * MIN(fish_GMCV, invertebrate_GMCV*10^{(0.028*(25-MAX(T,7)))})$$

The two species exhibiting the most sensitivity to ammonia at 25°C are invertebrates. The measure of sensitivity (GMCV) for invertebrates changes with temperature, however, becoming less at lower temperatures. The function describing the temperature response has a slope (0.028), a reference temperature (25°C), and low temperature cutoff (7°C); any one of these constants can be changed in AMMTOX. The effect of temperature on the sensitivity of fish to ammonia appears to be small or absent.

When ELS are present, the generalized equation can be simplified to yield equation 19 in the National Criteria document by recognizing that, below 14.5°C, the GMCV for *Hyalella* (1.45) is superseded by the GMCV for the ELS of *Lepomis* (2.85). The temperature cutoff in the generalized equation becomes superfluous. The resulting equation is:

$$CCC_{temperature} = 0.854 * MIN(2.85, 1.45*10^{(0.028*(25-T))})$$

When ELS are not present, the generalized equation can be simplified to yield equation 20 in the National Criteria document by recognizing that the fish GMCV (8.78) is too large to play a role. The GMCV for *Hyalella* continues to control the CCC even at low temperatures. The response of invertebrate GMCVs to temperature reaches a plateau at 7°C, below which the GMCV remains constant. The resulting equation is:

$$CCC_{temperature} = 0.854 * 1.45*10^{(0.028*(25-MAX(T,7)))}$$

The advantage of the rearrangement shown here is that the participation of the several terms is more transparent. The revised form of the equations does not change the output. AMMTOX sets default conditions for the CCC according to values presented in the National Criteria Document. Although it is possible in a technical sense to replace the fish GMCV or the invertebrate GMCV with alternative values, the user bears full responsibility for justifying those values and for assuring that they are implemented properly in AMMTOX.

USEPA Region 7 has a web page, http://www.epa.gov/Region7/water/sprt.htm#rule, that can facilitate the calculation of site-specific criteria.

Appendix B: Channel Geometry Equation data base, sorted by state

Steam	State	m	k	Slope	Drainage Area	Source
Sipsey River nr Elrod	AL	0.30			515	Leopold and Wolman, 1957
Tombigbee River nr Coatopa	AL	0.35			15500	Leopold and Wolman, 1957
Tombigbee River nr Leroy	AL	0.60			19100	Leopold and Wolman, 1957
Arkansas R. at Salida	CO	0.49			1218	Leopold and Wolman, 1957
Boulder Cr at 75th St	CO	0.45	0.21		304	Lewis and Saunders, unpublished
Boulder Cr at mouth	CO	0.36	0.35		439	Lewis and Saunders, unpublished
Boulder Cr near Orodell	CO	0.49	0.19		102	Lewis and Saunders, unpublished
Coal Cr at Louisville	CO	0.57	0.28		27	Lewis and Saunders, unpublished
South Platte at Ft Lupton	CO	0.18	0.86		5010	Lewis and Saunders, unpublished
South Platte at Henderson	CO	0.52	0.09		4713	Lewis and Saunders, unpublished
St Vrain at Lyons	CO	0.64	0.08		212	Lewis and Saunders, unpublished
St Vrain below Longmont	CO	0.27	0.56		424	Lewis and Saunders, unpublished
St Vrain nr Platteville	CO	0.22	0.64		976	Lewis and Saunders, unpublished
Cedar R at Janesville	IA	0.19			1660	Leopold and Wolman, 1957
Cedar R at Waterloo	IA	0.27			5190	Leopold and Wolman, 1957
Cedar R. at Cedar Rapids	IA	0.34			6640	Leopold and Wolman, 1957
Cedar R. nr Conesville	IA	0.22			7840	Leopold and Wolman, 1957
Iowa R. at Wapello	IA	0.41			12480	Leopold and Wolman, 1957
Lime R. at Mason City	IA	0.42			535	Leopold and Wolman, 1957
Shell Rock R. nr Northwood	IA	0.46			380	Leopold and Wolman, 1957
West Fork Shell Rock R at Finchford	IA	0.17			860	Leopold and Wolman, 1957
Big Bay Creek	IL	0.13	1.93	0.0004	226	Stall and Fok, 1968
Big Muddy	IL	0.16	2.62	0.0005	2323	Stall and Fok, 1968
Cornland	IL	0.27				Stall and Fok, 1968
Deland	IL	0.36				Stall and Fok, 1968
Des Plaines	IL	0.09	0.98	0.0003	137	Stall and Fok, 1968
Easton	IL	0.40				Stall and Fok, 1968
Embarras	IL	0.22	2.64	0.0014	2374	Stall and Fok, 1968
Embarras R. at St. Marie	IL	0.20			1540	Leopold and Wolman, 1957
Fox	IL	0.14	0.96	0.0010	2600	Stall and Fok, 1968
Galena	IL	0.07	1.13	0.0012	210	Stall and Fok, 1968
Greenview	IL	0.24				Stall and Fok, 1968
Harsburg	IL	0.33				Stall and Fok, 1968
Henderson Creek	IL	0.01	0.66	0.0008	602	Stall and Fok, 1968
Illinois R at Marseilles	IL	0.40			7640	Leopold and Wolman, 1957
Illinois R, at Kingston Mines	IL	0.54			15200	Leopold and Wolman, 1957
Illinois R. at Meredosia	IL	0.35			25300	Leopold and Wolman, 1957
Iroquois R. nr Chebanse	IL	0.35			2120	Leopold and Wolman, 1957
Kankakee	IL	0.18	1.92	0.0005	528	Stall and Fok, 1968
Kankakee R nr Wilmington	IL	0.46			5250	Leopold and Wolman, 1957
Kankakee R. at Momence	IL	0.38			2340	Leopold and Wolman, 1957
Kaskaskia	IL	0.13	1.55	0.0005	5815	Stall and Fok, 1968
Kincaid	IL	0.22				Stall and Fok, 1968
La Moine	IL	0.12	1.36	0.0012	1380	Stall and Fok, 1968
Lincoln	IL	0.20				Stall and Fok, 1968
Little Sandy Creek nr Elkhorn	IL	0.33			20.9	Leopold and Wolman, 1957
Little Wabash	IL	0.31	6.32	0.0007	2312	Stall and Fok, 1968
Macinaw	IL	0.09	0.90	0.0010	1173	Stall and Fok, 1968

Mohomet	IL	0.20				Stall and Fok, 1968
Monticello	IL	0.19				Stall and Fok, 1968
Nokomis	IL	0.35				Stall and Fok, 1968
Oakford	IL	0.28				Stall and Fok, 1968
Oakley	IL	0.29				Stall and Fok, 1968
Riverton	IL	0.27				Stall and Fok, 1968
Rochester	IL	0.17				Stall and Fok, 1968
Rock	IL	0.12	0.93	0.0009	10720	Stall and Fok, 1968
Rock R. at Coma	IL	0.45			8700	Leopold and Wolman, 1957
Rowell	IL	0.17				Stall and Fok, 1968
Sangamon	IL	0.25	3.12	0.0009	5452	Stall and Fok, 1968
Sangamon R. at Riverton	IL	0.15			2560	Leopold and Wolman, 1957
Sny	IL	0.24	2.02	0.0002	743	Stall and Fok, 1968
Spoon	IL	0.08	0.72	0.0010	1890	Stall and Fok, 1968
Springfield	IL	0.32				Stall and Fok, 1968
Taylorville	IL	0.15				Stall and Fok, 1968
Vermillion (Illionis Basin)	IL	0.17	1.61	0.0010	1315	Stall and Fok, 1968
Vermillion (Wabash Basin)	IL	0.30	3.36	0.0011	4110	Stall and Fok, 1968
Waynesville	IL	0.28				Stall and Fok, 1968
Kankakee R. at Davis	IN	0.14			506	Leopold and Wolman, 1957
Kankakee R. at Shelby	IN	0.29			1800	Leopold and Wolman, 1957
White River	IN	0.09	1.24			Stall and Fok, 1968
Kansas R. at Bonner Springs	KS	0.48			59890	Leopold and Wolman, 1957
Kansas R. at Lecompton	KS	0.25			58420	Leopold and Wolman, 1957
Kansas R. at Ogdon	KS	0.40			45240	Leopold and Wolman, 1957
Kansas R. at Topeka	KS	0.30			56710	Leopold and Wolman, 1957
Kansas R. at Wamego	KS	0.25			55240	Leopold and Wolman, 1957
Republican River at Clay Center	KS	0.20			24570	Leopold and Wolman, 1957
Saline River nr Russell	KS	0.25				Leopold and Maddock, 1953
Smokey Hill R. at Elkader	KS	0.30			3555	Leopold and Wolman, 1957
Smokey Hill R. at Enterprise	KS	0.72			19200	Leopold and Wolman, 1957
Smokey Hill R. at Lindsborg	KS	0.20			8110	Leopold and Wolman, 1957
Smoky Hill River at Ellsworth	KS	0.26			7580	Leopold and Maddock, 1953
Smoky Hill River near Ellis	KS	0.16			5630	Leopold and Maddock, 1953
Connecticut R. at Montague City	MA	0.46			7865	Leopold and Wolman, 1957
Antietam Creek nr Sharpsburg	MD	0.57			281	Leopold and Wolman, 1957
Missouri River at Herman	MD	0.50			528200	Leopold and Wolman, 1957
NW branch of Anacostia River nr Colesville	MD	0.42			21	Leopold and Wolman, 1957
Seneca Cr at Riffleford nr Rockville	MD	0.30			100	Leopold and Wolman, 1957
Watts Branch, Viers pasture nr Rockville	MD	0.50			4.2	Leopold and Wolman, 1957
Cedar River nr Austin	MN	0.39			425	Leopold and Wolman, 1957
Turtle Creek br Austin	MN	0.29			144	Leopold and Wolman, 1957
Missouri River at Kansas City	MO	0.37			489200	Leopold and Wolman, 1957
Missouri River at St. Joeseph	MO	0.58			424300	Leopold and Wolman, 1957
Buttahatchee River nr Caledonia	MS	0.75			823	Leopold and Wolman, 1957
Tombigbee River at Aberdeen	MS	0.38			2210	Leopold and Wolman, 1957
Tombigbee River nr Columbus	MS	0.52			4490	Leopold and Wolman, 1957
Bighorn R. near Custer	MT	0.40			22350	Leopold and Wolman, 1957
Clark Fork near Edgar	MT	0.60			2115	Leopold and Wolman, 1957
Clark Fork R. above Missoula	MT	0.51			5740	Leopold and Wolman, 1957
Clark Fork R. at St. Regis	MT	0.44			10500	Leopold and Wolman, 1957
Clark Fork R. nr Heron	MT	0.36			21800	Leopold and Wolman, 1957
Clark Fork R. nr Plains	MT	0.69			19900	Leopold and Wolman, 1957
Clark Fork R.below Missoula	MT	0.77			8690	Leopold and Wolman, 1957
Flathead R. at Columbia Falls	MT	0.55			4464	Leopold and Wolman, 1957
Flathead R. nr Columbia Falls	MT	0.38			1553	Leopold and Wolman, 1957
Flathead R. nr Polson	MT	0.50			7096	Leopold and Wolman, 1957
Little Bighorn R at State line nr Wyola	MT	0.64			199	Leopold and Wolman, 1957
Little Bighorn R. below Pass Cr. Nr Wyola	MT	0.45			429	Leopold and Wolman, 1957
Little Bighorn R. nr Crow Agency	MT	0.50			1190	Leopold and Wolman, 1957

Missouri R at Toston	MT	0.48				Leopold and Wolman, 1957
Pend Oreille R. below Z Canyon nr Metaline Falls	MT	0.34			25200	Leopold and Wolman, 1957
Powder River near Locate	MT	0.30			12900	Leopold and Wolman, 1957
Rock Creek near Red Lodge	MT	0.71			100	Leopold and Wolman, 1957
West Fork Rock Creek below Basin Cr. Br Red Lodge	MT	0.58			60	Leopold and Wolman, 1957
Yellowstone River at Billings	MT	0.46			11600	Leopold and Wolman, 1957
Yellowstone River at Corwin Springs	MT	0.45			5630	Leopold and Wolman, 1957
Yellowstone River nr Sidney	MT	0.58			69450	Leopold and Wolman, 1957
Catheys Cr. Nr Brevard	NC	0.67			11.7	Leopold and Wolman, 1957
Davidson R near Brevard	NC	0.53			40.4	Leopold and Wolman, 1957
French Broad River at Bent Cr.	NC	0.47			676	Leopold and Wolman, 1957
French Broad River at Rosman	NC	0.45			67.9	Leopold and Wolman, 1957
French Broad Riverat Calvert	NC	0.45			103	Leopold and Wolman, 1957
Noland Cr. Nr Bryson City,	NC	0.65			13.8	Leopold and Wolman, 1957
Watauga R. Nr Surgar Grove	NC	0.50			90.8	Leopold and Wolman, 1957
Missouri River at Bismark	ND	0.45			186400	Leopold and Wolman, 1957
Arikaree River at Haigler	NE	0.30			1460	Leopold and Wolman, 1957
Middle Loup River at Arcadia	NE	0.35				Leopold and Maddock, 1953
Middle Loup River at St. Paul	NE	0.37				Leopold and Maddock, 1953
N. Platte nr Keystone	NE	0.15			30000	Leopold and Wolman, 1957
N. Platte River nr Lisco	NE	0.21			26900	Leopold and Wolman, 1957
N. Platte River nr Mitchell	NE	0.12			24300	Leopold and Wolman, 1957
N. Platte River nr N. Platte	NE	0.18			32000	Leopold and Wolman, 1957
N. Platte River nr Sutherland	NE	0.20			31300	Leopold and Wolman, 1957
Platte River nr Grand Island	NE	0.22			59500	Leopold and Wolman, 1957
Platte River nr Odessa	NE	0.23			58800	Leopold and Wolman, 1957
Platte River nr Overton	NE	0.27			58400	Leopold and Wolman, 1957
Republican River at Bloomington	NE	0.44		0.0360	20800	Leopold and Maddock, 1953
Republican River at Bloomington	NE	0.40			20800	Leopold and Wolman, 1957
S. Platte at Paxton	NE	0.22			23700	Leopold and Wolman, 1957
Connecticut River at First Connecticut Lake nr Pittsburgh	NH	0.56			83	Leopold and Wolman, 1957
Connecticut River at N. Stratford	NH	0.58			799	Leopold and Wolman, 1957
Connecticut River nr Dalton	NH	0.42			1514	Leopold and Wolman, 1957
Ancha Chiquita nr El Rancho Montoso S of Santa Fe	NM	0.32			0.09	Leopold and Wolman, 1957
Arroryo de las Chamisos nr Mt. Carmel Chapel at Santa Fe	NM	0.26			2.5	Leopold and Wolman, 1957
Canada Ancha nr El Rancho Montoso br Santa Fe	NM	0.28			1.52	Leopold and Wolman, 1957
Rio Galisteo at Cerrillos	NM	0.29			100	Leopold and Wolman, 1957
Rio Galisteo at Comingo	NM	0.24			600	Leopold and Wolman, 1957
Rio Grande at San Acacia	NM	0.28				Leopold and Maddock, 1953
Rio Grande at San Felipe	NM	0.30				Leopold and Maddock, 1953
Rio Grande near Bernalillo	NM	0.51				Leopold and Maddock, 1953
Rio Puerco at Cabezon	NM	0.34				Leopold and Wolman, 1957
Rio Puerco at Rio Puerco	NM	0.41				Leopold and Maddock, 1953
Rio Puerco nr Cabezon	NM	0.36			360	Leopold and Wolman, 1957
Rio Santa Fe at Old Albuquerque Rd west of Santa Fe	NM	0.35			175	Leopold and Wolman, 1957
Tributary to Hermanas Arroyo nr Las Dos NW of Santa Fe	NM	0.43			0.06	Leopold and Wolman, 1957
Auplaize R. nr Defiance	OH	0.45			2329	Leopold and Wolman, 1957
Blanchard R at Glendorf	OH	0.32			643	Leopold and Wolman, 1957
Blanchard R. nr Findlay	OH	0.28			343	Leopold and Wolman, 1957
Maumee R at Antwerp	OH	0.22			2049	Leopold and Wolman, 1957
Maumee R at Waterville	OH	0.50			6314	Leopold and Wolman, 1957
Maumee R nr Defiance	OH	0.38			5530	Leopold and Wolman, 1957
Ottawa R. at Allentown	OH	0.28			168	Leopold and Wolman, 1957
Ottawa R. at Kalida	OH	0.40			315	Leopold and Wolman, 1957

Scioto R. at Chillicothe	OH	0.53			3847	Leopold and Wolman, 1957
Scioto R. at Columbus	OH	0.46			1624	Leopold and Wolman, 1957
Scioto R. at La Rue	OH	0.50			255	Leopold and Wolman, 1957
Scioto R. Nr Circleville	OH	0.64			2635	Leopold and Wolman, 1957
Scioto R. nr Dublin	OH	0.40			988	Leopold and Wolman, 1957
Scioto R. nr Prospect	OH	0.42			571	Leopold and Wolman, 1957
Tiffin River at Stryker	OH	0.43			444	Leopold and Wolman, 1957
Shaver Creek	PA	0.21	1.90			Brush, 1961
Bald Eagle Creek	PA	0.25	1.25			Brush, 1961
Beech Creek	PA	0.00	12.00			Brush, 1961
Brandywine Creek at Chadds Ford	PA	0.42				Wolman 1955
Brandywine Creek at Coatesville	PA	0.48				Wolman 1955
Brandywine Creek at Cornog	PA	0.52		0.0034	25.7	Wolman 1955
Brandywine Creek at Embreeville	PA	0.59		0.0005	117	Wolman 1955
Brandywine Creek at Georgia	PA	0.69		0.0004	118	Wolman 1955
Brandywine Creek at Lenape	PA	0.46		0.0007	259	Wolman 1955
Brandywine Creek at Seven Springs	PA	0.48		0.0025	54.2	Wolman 1955
Brandywine Creek at South Downington	PA	0.61		0.0008	86	Wolman 1955
Brandywine Creek at Wawaset	PA	0.53		0.0009	134	Wolman 1955
Buffalo Run	PA	0.00	20.00			Brush, 1961
Fishing Creek	PA	0.00	18.00			Brush, 1961
Globe Run	PA	0.29	1.80			Brush, 1961
Honey Creek	PA	0.28	1.55			Brush, 1961
Little Juniata River	PA	0.07	2.60			Brush, 1961
Marsh Creek	PA	-0.51	220.00			Brush, 1961
McClain Run	PA	0.00	4.30			Brush, 1961
Reeds Run	PA	-0.06	4.80			Brush, 1961
Sixmile Creek	PA	0.16	2.80			Brush, 1961
Slab Cabin Creek	PA	0.29	1.75			Brush, 1961
Standing Stone Creek	PA	0.10	4.30			Brush, 1961
Warriors Mark Creek	PA	-0.05	18.50			Brush, 1961
Weiker Run	PA	-0.18	20.00			Brush, 1961
Belle Fourch R. nr Elm Springs	SD	0.32			7210	Leopold and Wolman, 1957
Cheyenne River nr Hot Springs	SD	0.25			7.3	Leopold, 1953
Grand River Shadehill	SD	0.39				Leopold and Maddock, 1953
Missouri River at Pierre	SD	0.47			243500	Leopold and Wolman, 1957
Moreau River near Faith	SD	0.34				Leopold and Maddock, 1953
White River nr Ogala	SD	0.07				Leopold and Maddock, 1953
French Broad River nr Newport	TN	0.65			1858	Leopold and Wolman, 1957
Tennessee River at Knoxville	TN	0.28			8934	Leopold and Wolman, 1957
Virgin River at Virgin	UT	0.45				Leopold and Maddock, 1953
Cedar Creek bear Winchester	VA	0.35			101	Leopold and Wolman, 1957
Middle R near Grottoes	VA	0.53			360	Leopold and Wolman, 1957
N. Fork Shenandoah R at Cootes Store	VA	0.42			215	Leopold and Wolman, 1957
N. Fork Shenandoah R near Strasburg	VA	0.35			772	Leopold and Wolman, 1957
N. Fork Shenandoah R. at Mt Jackson	VA	0.52			509	Leopold and Wolman, 1957
Passage Creek at Buckton	VA	0.47			87	Leopold and Wolman, 1957
South Fork Shenandoah R. at Front Royal	VA	0.54			1638	Leopold and Wolman, 1957
South Fork Shenandoah R. near Luray	VA	0.59			1377	Leopold and Wolman, 1957
South Fork Shenandoah R. near Lynnwood	VA	0.38			1076	Leopold and Wolman, 1957
South R at Harriston	VA	0.60			222	Leopold and Wolman, 1957
South R at Waynesboro	VA	0.50			144	Leopold and Wolman, 1957
Stony Creek at Columbia Furnace	VA	0.31			76	Leopold and Wolman, 1957
Connecticut River nat White R. Junction	VT	0.30			4092	Leopold and Wolman, 1957
White River nr Bethel	VT	0.36			241	Leopold and Wolman, 1957
White River at West Hartford	VT	0.57			690	Leopold and Wolman, 1957
White River	WA	0.27	1.10			Fahnestock, 1963
Shenandoah R at Millville	WV	0.56			3040	Leopold and Wolman, 1957
Beaver Cr. Nr Danial	WY	0.50			141	Leopold and Wolman, 1957
Belle Fourche R. at Hulett	WY	0.45			2800	Leopold and Wolman, 1957

Belle Fourche River below Moorcroft	WY	0.25			1730	Leopold and Maddock, 1953
Belle Fourche River below Moorcroft	WY	0.28			1730	Leopold and Wolman, 1957
Big Horn R at Thermopolis	WY	0.59			8080	Leopold and Wolman, 1957
Big Horn River at Kane	WY	0.43			15900	Leopold and Maddock, 1953
Big Horn River at Manderson	WY	0.35			11900	Leopold and Wolman, 1957
Bighorn R at Kane	WY	0.43			15900	Leopold and Wolman, 1957
Bighorn River at Manderson	WY	0.28			11900	Leopold and Maddock, 1953
Bighorn River at Thermopolis	WY	0.55			8080	Leopold and Maddock, 1953
Boulder Cr. Below Boulder Lake nr Boulder	WY	0.47			130	Leopold and Wolman, 1957
Bull Lake Creek near Lenore	WY	0.50			222	Leopold and Wolman, 1957
Clear Creek nr Buffalo	WY	0.48			120	Leopold and Wolman, 1957
East Fork River nr Big Sandy River	WY	0.50			79.2	Leopold and Wolman, 1957
Fontenelle Creek near Fontenelle	WY	0.50			224	Leopold and Wolman, 1957
Gooseberry Cr. Nr Grass Creek	WY	0.43			155	Leopold and Wolman, 1957
Green R nr Fontenelle	WY	0.60			3970	Leopold and Wolman, 1957
Green River at Warren bridge nr Danial	WY	0.52			468	Leopold and Wolman, 1957
Greybull River nr Basin	WY	0.37			1130	Leopold and Wolman, 1957
Greybull River nr Meeteetse	WY	0.35			690	Leopold and Wolman, 1957
Horse Creek nr Danial	WY	0.44			124	Leopold and Wolman, 1957
Lance Creek Creek at Spencer	WY	0.34			2070	Leopold and Wolman, 1957
Laramie River nr Ft. Laramie	WY	0.40			4600	Leopold and Wolman, 1957
Little Popo Agie nr Lander	WY	0.47			108	Leopold and Wolman, 1957
Medicine Lodge Cr. Nr Hyattville	WY	0.52			86	Leopold and Wolman, 1957
Meet John Wash nr Casper	WY	0.45				Leopold and Wolman, 1957
Middle Pinny Cr. Below S. Fork nr Big Pinny	WY	0.48			34.3	Leopold and Wolman, 1957
N. Fork Owl Cr. Nr Anchcr	WY	0.47			58.2	Leopold and Wolman, 1957
N. Fork Popo Agie River nr Lander	WY	0.65			140	Leopold and Wolman, 1957
N. Piney Creek nr Mason	WY	0.42			58	Leopold and Wolman, 1957
N. Platte at Saratoga	WY	0.57			2880	Leopold and Wolman, 1957
N. Platte below Casper	WY	0.20			12600	Leopold and Wolman, 1957
N. Platte below Whalen	WY	0.32			16350	Leopold and Wolman, 1957
N. Platte nr Douglas	WY	0.28			14300	Leopold and Wolman, 1957
N. Platte R at WY-NE State line	WY	0.16			22100	Leopold and Wolman, 1957
New Fork R. near Boulder	WY	0.30			552	Leopold and Wolman, 1957
Owl Creek nr Thermopolis	WY	0.50			484	Leopold and Wolman, 1957
Pecatpmoca R. at Freeport	WY	0.43			1330	Leopold and Wolman, 1957
Popo Agie R. nr Riverton	WY	0.62			2010	Leopold and Wolman, 1957
Powder R. at Arvada	WY	0.29			6050	Leopold and Wolman, 1957
Powder R. at Sussex	WY	0.30			3090	Leopold and Wolman, 1957
Powder River at Arvada	WY	0.31		0.0009	6050	Leopold and Maddock, 1953
Silver Cr nr Big Sandy	WY	0.27			45.4	Leopold and Wolman, 1957
South Fork Owl Creek abouve Curtis ranch at Thermopolis	WY	0.52			139	Leopold and Wolman, 1957
Wind River at Crowheart	WY	0.40			1920	Leopold and Wolman, 1957
Wind River at Riverton	WY	0.31			2320	Leopold and Wolman, 1957
Wind River nr Burris	WY	0.62			1220	Leopold and Wolman, 1957
Wind River nr Dubious	WY	0.59			233	Leopold and Wolman, 1957