Improvements in Stream Ammonia Models by Simultaneous Computation of Extremes in Flow and Water Chemistry

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For wastewater discharge permits, it is standard practice to assume that critical conditions of low flow will coincide with conditions of pH and temperature that maximize the un-ionized fraction of ammonia. The present study reports the results of an analysis of this association at 12 sites in Colorado. The study shows no general relationship between flow and percent un-ionized ammonia at any station. Also, within periods of low flow there is no parametric association between percent un-ionized ammonia and low flow. A nonparametric test focusing specifically on periods of low flow shows that eight of the stations have a random association of the two variables, three stations have percent un-ionized ammonia significantly lower than the mean during periods of low flow, and a single station has percent un-ionized ammonia above the mean during low flows. Overall, the assumption of strong association between low flow and high percent un-ionized ammonia is not justified by field data and may result in overly stringent ammonia control requirements for point source discharges.

Introduction

The quantity of un-ionized ammonia in surface waters of the United States is regulated for the protection of aquatic life (*1*). Regulation is achieved primarily through NPDES permits under jurisdiction of the Clean Water Act. Even when extensive information is available on flow and water chemistry, the computation of allowable ammonia discharge limits is complicated by a variety of factors including dilution, mixed temperature and pH at the point of discharge, decay of ammonia below the point of discharge as a result of biological conversion, change in pH and temperature below the point of discharge, and 24-h or seasonal cycles in pH, temperature, and biological processes.

The establishment of limits for total ammonia in point-source discharges is so complicated that it cannot be accomplished reliably without the use of models that take into account the numerous processes influencing concentrations of total ammonia in the stream. A further complication is the partitioning between ionized and un-ionized fractions of ammonia. Un-ionized ammonia is the direct basis for water quality standards, but permits are based on total ammonia. The connection between total and un-ionized ammonia depends on pH, temperature, and dilution.

The maximum total ammonia that can be allowed for a discharge of given size in a particular month depends on two sets of critical conditions, one of which is related to flow and the other to water quality. Traditionally, these two sets of critical conditions are calculated separately and then brought together in the final estimate of maximum allowable total ammonia. For flow, the relevant condition for the setting of limits on total ammonia is typically the critical low flow in the receiving water, i.e., the condition of least dilution. In many states, and for the U.S. EPA, the critical low flow is the biologically based low flow (DFLOW) as defined by the U.S. EPA (*2*). Other states may use hydrologically based low flows such as the 7-d, 10-yr low flow, but the effect is the same: the critical low flow is calculated for a given month or block of months on the basis of the hydrologic record.

For water quality, the critical condition is determined by the simultaneous effect of pH and temperature on the percent of ammonia that is un-ionized. The percent of total ammonia that is un-ionized increases directly in response to increase in pH or temperature (*3*). The relationship of pH and temperature to the ionization of ammonia is given by

$$f = 1/(10^{pK_a\text{-}pH} + 1)$$

where f is the fraction of ammonia in un-ionized form, $pK_a = 0.09018 + 2729.92/T$ and T is temperature (K) (*3*).

The regulatory authority sets critical concentrations for un-ionized ammonia and specifies a critical probability of exceedence for these concentrations; in many states and in the National Criteria, the probability corresponds to a 3-yr return frequency. From the exceedence probability, the corresponding combinations of pH and temperature

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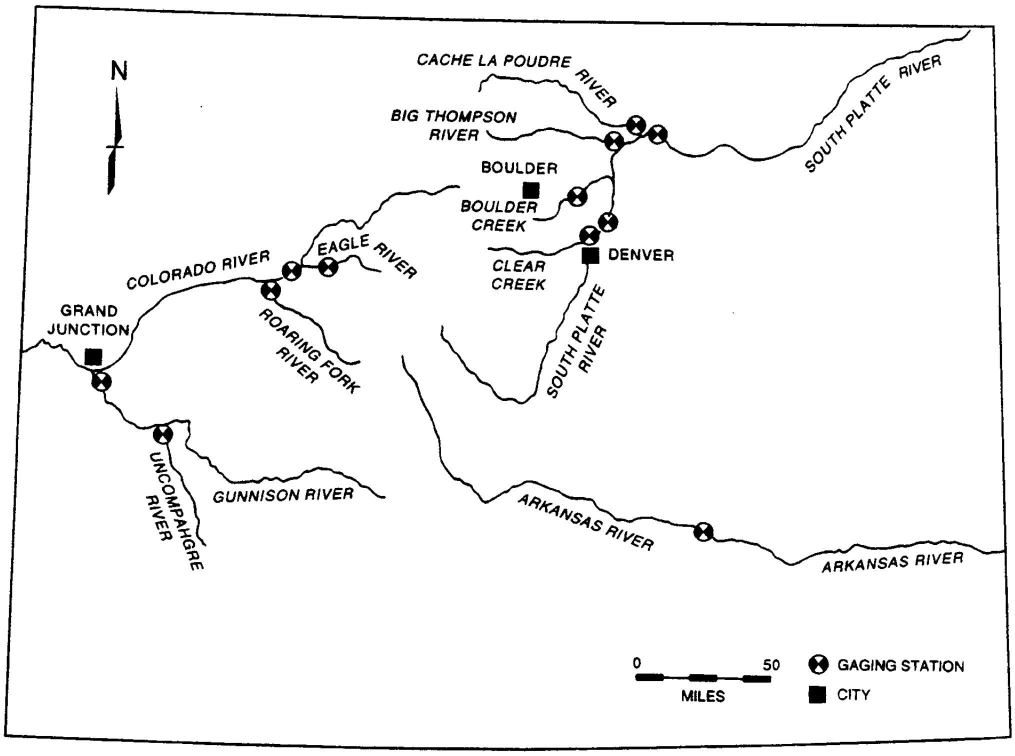

FIGURE 1. Map of the state of Colorado showing the approximate locations of the 12 stations that were used in the study.

for a given month can be calculated from models (e.g., refs 4 and 5), or they can be roughly approximated by other means if no model is used. In either case, the result is a critical set of pH and temperature combinations for each month. These combinations, with their corresponding values for percent un-ionized ammonia, are brought together with the critical low flow in calculating the maximum total ammonia for discharge to the stream that would be consistent with the standard.

The implicit assumption in combining the critical low flow with the combinations of pH and temperature producing extreme percentages of un-ionized ammonia is that the least favorable conditions for both sets of variables will occur simultaneously. This is a conservative assumption from the viewpoint of water quality protection, but it is not necessarily correct. For example, if flows are in reality associated randomly with pH and temperature, it would not be necessary to combine the critical low flow with the critical pH and temperature for a given month. In effect, the assumption of perfect correlation between critical combinations of pH and temperature and critical low flows will penalize the discharger unnecessarily if the two sets of variables are not correlated or if they are only weakly correlated. The result could be excessive expenditures on nitrification or, from the regulatory point of view, overemphasis on the regulation of ammonia at the expense of possible improvement of water quality through regulation of other substances.

The purpose of the present study is to report the result of an empirical study of the relationship between critical combinations of pH and temperature and critical low flows in the state of Colorado. The study is designed to establish a foundation for adding a new level of realism to water quality models. More generally, however, the results will be of interest in support of any attempt to set realistic limits on ammonia discharges in compliance with a numeric standard. Beyond the regulation of total ammonia, the general topic of correlation between extremes of flow and extremes of water chemistry or water temperature has numerous practical implications.

Design and Methods of the Study

The study relies on analysis of concurrent records for flow, pH, and temperature in waters of Colorado. Because the underlying question is a probabilistic one, the duration of the record is important. The following criteria were used in the selection of stations for the study: (1) gaged flows on a daily basis extending from 1970 to 1991, (2) water quality measurements on at least a monthly basis between 1970 and 1991, and (3) coverage of temperature and pH. Within the state of Colorado, 12 stations satisfy these criteria through the monitoring programs of the Colorado Department of Health Water Quality Control Division (Figure 1).

Hydrologic records were assembled for each of the 12 stations. Data for each station were then processed with the U.S. EPA's DFLOW algorithm to produce the biologically based low flow estimates for 1- and 30-d averaging periods (acute and chronic critical flows in Colorado). The absolute minimum flows were also obtained for each month of the year over the entire period of record.

The water quality measurements in all cases were from grab samples taken weekly, biweekly, or monthly. The flow corresponding to each water quality measurement was established for each station by use of the hydrologic data base. The number of dates for water quality samples varied between 132 for the Roaring Fork and 422 for the South Platte (median, 340).

Data on pH and temperature are based on grab samples taken during the daylight hours (more than 80% between 0900 and 1500). Both pH and temperature show a 24-h cycle; daytime sampling would coincide with the highest values of the cycle and thus with the highest (least favorable)

TABLE 1

Mean Discharge and Biologically Based Low Flow at Each of the 12 Stations and Number of Days in the Discharge Record between 1970 and 1991 for Which the Discharge Was Less Than or Equal to the 1-d Threshold Value for Biologically Based Low Flow[a]

USGS station	discharge (m^3/s) mean	DFLOW acute	DFLOW chronic	DFLOW, acute total days	months of occurrence	un-ionized ammonia mean % un-ionized	months of extremes	no. of extremes
Clear Creek near mouth	2.9	0.02	0.08	7	3, 4, 12	4.1	3–5, 7–10	28
South Platte at Henderson	16.8	1.80	3.74	9	2, 3	63.8	6, 8	2
Boulder Creek at county line	2.1	0.06	0.14	6	1, 10, 12	6.9	2–12	85
Big Thompson near mouth	3.6	0.04	0.29	5	4, 6	2.6	2, 4–8	8
Cache la Poudre near Greeley	6.1	0.19	0.43	3	5	2.0	4–8	6
South Platte near Kersey	35.9	1.98	4.10	15	4, 5	2.2	3, 7, 8, 12	5
Arkansas near Nepesta	20.7	1.24	2.60	7	8, 11	2.8	4–6, 8, 9, 12	9
Eagle at Gypsum	16.4	3.02	3.96	13	2, 8, 9, 11	4.5	7–9	9
Colorado near Dotsero	61.2	15.44	18.84	7	2, 3, 4, 11, 12	3.7	6–10	17
Roaring Fork at mouth	34.8	7.78	9.51	10	3, 4, 8	5.3	1–4, 6–9, 11	18
Uncompahgre River at delta	9.0	1.44	2.37	12	3, 4	3.2	2, 3, 5, 8, 9	6
Gunnison River near Grand Junction	74.5	13.03	16.58	15	4, 7, 8	5.7	3, 4, 6–11	17

[a] The table also shows mean percent un-ionized ammonia (1970–1991), months in which these values exceeded 10% (extremes of un-ionized ammonia), and number of dates for values over 10%.

percent un-ionized ammonia. The variation across seasons or months exceeds greatly the variation in pH or temperature during the midday hours of a given day for Colorado streams (*4*). For this reason, variations in the time of day for collection of grab samples is unlikely to affect the statistical analysis of relationships between un-ionized ammonia and discharge.

As indicated by Table 1, critical concentrations of un-ionized ammonia could occur in any month because low flows and extremes of percent un-ionized ammonia occur over a wide range of months, even for specific sites. Temperature and pH tend to be highest in warm months, but because nitrification is lowest in cool months, extremes of un-ionized ammonia can occur even in cool or cold months.

The combined information including daily flows, critical low flows as defined by DFLOW, and the entire record of pH and water temperature measurements with the corresponding flows on the date of sampling provide the foundation for analysis of the relationship between flow and percent un-ionized ammonia as determined by pH and temperature. The main focus of the analysis is on extremes of low flow and their association with extreme values of percent un-ionized ammonia.

Results

Discharge. As expected, the frequency distributions of discharge for all 12 stations show strong positive skew when plotted on an arithmetic scale (i.e., the discharge tends to be log-normally distributed). Mean discharges (Table 1) vary from 74 m^3/s for the Gunnison River southeast of Grand Junction to 2.1 m^3/s for Boulder Creek at County Line Road. The statistics represent a wide range of drainage areas (264–24 860 km^2). The stations are broadly distributed over the state, represent a variety of elevations (1405–1913 m above sea level), and reflect varying degrees of hydrographic control through diversion. All stations are influenced by some combination of transmountain diversions, storage reservoirs, and irrigation withdrawals, which are typical of Colorado and of the western United States.

Table 1 gives the low-flow (DFLOW) values for each of the stations and shows the total number of days for which the flow was equal to or less than the low flow and the months during which low flows were observed. The table shows that the 12 streams collectively have critical flows in all 12 months of the year. As a result of the complex interaction between seasonal runoff and diversions, most streams show critical low flows in more than one season. Seasonally, the 1-d minimum low flows were distributed as follows for the entire data set: winter (DJF), 10%; spring (MAM), 49%; summer (JJA), 23%; fall (SON), 18%. Overall, Table 1 indicates that the breadth of hydrologic conditions represented among the 12 sites for the low-flow analysis is very great and, thus, is ideally suited for an exploration of the connection between low flow and water quality under a variety of conditions.

Relationships among various measures of low flow were explored statistically. There is a close relationship between the minimum 30-d flow and the minimum 1-d flow across the entire record for any given month (r^2 = 0.98–0.99 for logarithmically transformed data). In addition, the 30-d DFLOW value is very closely related to the 1-d DFLOW value. The relationship between DFLOW and mean discharge is considerably weaker, although it is significant statistically (r^2 = 0.86–0.90 for logarithmically transformed data).

Water Quality. The water quality variable of direct concern in computing the total ammonia allowance for a stream is percent un-ionized ammonia, which is under direct control of pH and temperature. For each sampling date at each station, the information on pH and temperature was used in calculating percent un-ionized ammonia. Un-ionized ammonia in excess of 10% of total ammonia was taken as an arbitrary indicator of extreme values. The data show a wide range in the number of extreme values (Table 1), reflecting contrasts in the range of pH and temperature combinations across the 12 stations. The highest values for percent un-ionized ammonia are scattered across a wide range of discharges at all of the stations.

Table 1 also gives the mean percent un-ionized ammonia at each of the stations and shows the distribution of most extreme values across months of the year for each station. The extremes can be found for at least one of the sampling stations in any month of the year. The highest number of

TABLE 2

Summary of Information on Un-ionized Ammonia and Discharge at Times of Low Discharge (Discharge below Fifth Percentile at Each Station)[a]

station name	mean discharge (cfs)	SD	no.	mean % un-ionized	SD	r^2	χ^2	r^2 (month) for significant associations
Clear Creek near mouth	0.07	0.02	17	8.1	11	0.00	3.8	
South Platte at Henderson	4.00	0.66	23	0.9	0.6	0.45*	0.2	
Boulder Creek at county line	0.15	0.04	13	3.8	5.9	0.28	1.0	0.14 (4), 0.16 (7)
Big Thompson near mouth	0.46	0.22	20	4.2	1.7	0.01	8.1*	
Cache la Poudre near Greeley	0.41	0.11	21	2.3	1.7	0.01	2.9	0.24 (1)
South Platte near Kersey	4.26	1.03	23	4.3	2.9	0.02	9.6*	0.21 (5), 0.20 (6)
Arkansas near Nepesta	2.73	0.63	22	3.7	4.9	0.00	2.3	0.19 (1), 0.29 (2)
Eagle at Gypsum	4.05	0.13	7	4.0	4.6	0.28	3.5	
Colorado near Dotsero	19.53	1.00	20	1.5	0.8	0.03	8.1*	0.19 (5), 0.23 (6), 0.17 (8)
Roaring Fork at mouth	9.60	0.96	10	6.6	5.6	0.21	0.0	0.72 (2)
Uncompahgre at delta	2.43	0.30	13	3.3	3.1	0.05	6.5*	0.21 (5), 0.16 (6)
Gunnison southeast of Grand Junction	17.03	2.19	13	7.6	2.4	0.09	3.1	0.43 (4), 0.47 (6), 0.62 (8)

[a] Mean discharge for values is shown along with its standard deviation, as is the number of points falling below the fifth percentile for discharge. The mean percent un-ionized ammonia is shown in the fifth column, followed by its standard deviation. The value of r^2 indicates the result of a regression analysis of the discharge and percent un-ionized ammonia at times of low discharge, and the χ^2 value indicates the result of a test of association for percentile values of un-ionized ammonia for dates falling within the fifth percentile for discharge. The last column shows the results of a parametric test of association between precent un-ionized ammonia and discharge at low flows (below fifth percentile) for individual months; only statistically significant associations are shown ($p \leq 0.05$). An asterisk (*) indicates that association is significant at $r = 0.05$.

extreme values however occurs in the warm months of the year. This reflects partly the influence of temperature on un-ionized ammonia, but equally important or more important is the occurrence of high rates of photosynthesis, which tends to drive up the pH during the warmer months. November, December, and January show the smallest incidence of extreme values for percent un-ionized ammonia.

General Relationships between Discharge and Percent Un-ionized Ammonia. Scatter plots of percent un-ionized ammonia in relation to flow do not suggest any general relationship between percent un-ionized ammonia and flow. This is confirmed by statistical analysis: following logarithmic transformation to improve bivariate normality, the two variables show no significant relationship for any station.

The analysis of relationships between percent un-ionized ammonia and flow was repeated for individual months on grounds that relationships for individual months might be obscured when the months are combined. Only a few relationships are significant, and all of these proved to be quantitatively weak (Table 2).

Percent Un-ionized Ammonia at Times of Low Flow. Two approaches were taken to the analysis of association between flow and percent un-ionized ammonia focusing on low flow: (1) parametric regression analysis of the association between percent un-ionized ammonia and discharge under low-flow conditions and (2) a nonparametric analysis of the association between percent un-ionized ammonia and low-flow conditions. The parametric test explores associations within the low-flow period, and the nonparametric test contrasts the low-flow period with all other time intervals.

The regression analysis for each station was confined to flows less than or equal to the fifth percentile. This resulted in the selection of 7–23 sampling dates for each station depending on the frequency of water quality sampling for the station (Table 2). For each date of low flow at each station, the corresponding percent un-ionized ammonia was calculated from the pH and temperature data. Percent un-ionized ammonia was then regressed against discharge for each station. Table 2 summarizes the results. In only one instance (South Platte at Kersey) was there a significant association between discharge and percent un-ionized ammonia for dates showing discharges at or below the fifth percentile of discharge.

The second test of association between discharge and percent un-ionized ammonia also involves the selection of dates on which the discharge was equal to or below the fifth percentile and the computation of the percent un-ionized ammonia for each of these dates at each station. In addition, a cumulative percentile value for percent un-ionized ammonia was calculated for each date at each station based on ranked values for the entire record at a given station. The following hypothesis was then formulated for testing at each station: When the discharge is equal to or below the fifth percentile for the entire data record, the percentile rank for percent un-ionized ammonia will be higher than for a random sample taken from the entire data set. In other words, when flow is very low, an association of flow and high percent un-ionized ammonia will show up in terms of a percentile rank for un-ionized ammonia that is significantly above the 50th percentile. This hypothesis was tested nonparametrically by use of the χ^2 statistic. For a given number of data records below the fifth percentile of flow, the expectation for random association is that half of the observed values for un-ionized ammonia will be above the 50th percentile and half will be below. The observed can be compared with this expectation by use of the χ^2 statistic.

Table 2 summarizes the results of the χ^2 test. Eight of the 12 stations show no significant deviation from a random association between low discharge and percent un-ionized ammonia. Four stations do show a statistically significant deviation (at $\alpha = 0.05$), but three of these associations are the inverse of the association postulated by the working hypothesis, i.e., the percentile rank of un-ionized ammonia at times of low flow for three of the 12 stations is significantly below the 50th percentile for the entire data record. The single significant association of the type predicted by the working hypothesis is for the South Platte River near Kersey.

The χ^2 test was repeated for the composite of low-flow values at all stations. This test showed no association

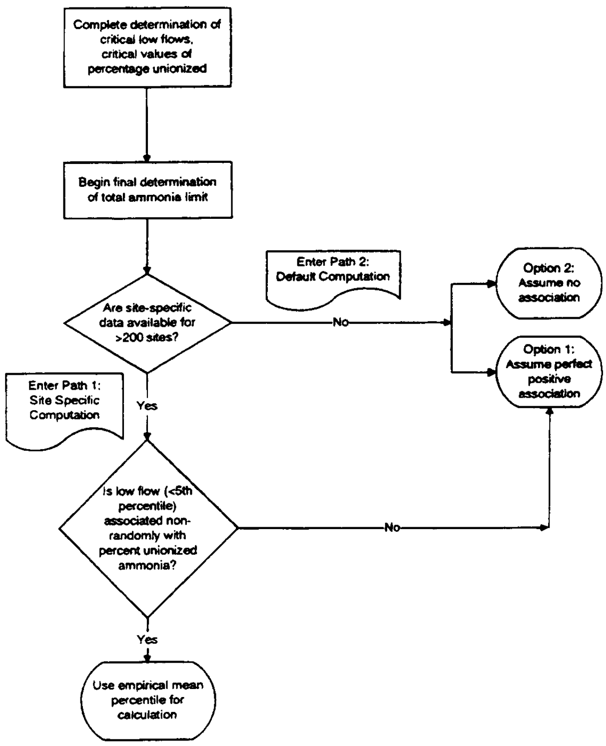

FIGURE 2. Decision diagram for treatment of the relationship between low flow and percent un-ionized ammonia.

between low flow and percentile rank of un-ionized ammonia values across all dates.

Discussion and Interpretation

The standard assumption for regulatory practice is that critical low flows are statistically associated with critical conditions for percent un-ionized ammonia. For a wide assortment of stations in the state of Colorado, this assumption is incorrect. The most accurate general assumption, in the absence of data for any particular station, would be that there is no association whatsoever between low flow and extreme conditions of percent un-ionized ammonia. The assumption of a perfect association leads to limitations on discharge concentrations that are considerably stricter than required by state or national criteria for recurrence of critical values (3-yr average recurrence).

The absence of strong associations between low flow and extreme conditions for percent un-ionized ammonia opens several possibilities for preparation of NPDES permits. After the critical low-flow values and critical percent un-ionized ammonia values have been established for each month, standard procedure would dictate straightforward combination of these values to calculate for each month the total ammonia allowance for the discharge. However, the findings of the present study suggest, at least for Colorado, a more logical way to proceed as shown in Figure 2. The first decision is based on the distinction between sites for which extensive information is available and sites for which less information is available. Without approximately 200 data points for water quality and discharge, the basis for a statistical determination of association between percent un-ionized ammonia and low flow is weak. If a large data base is available, as it is for some long-term monitoring sites, a site-specific determination can be made. This site-specific determination can be based upon an approach similar to the one that was used for the 12 stations of this study, i.e., a nonparametric test of association. If a statistically significant association is present, the mean percentile value for un-ionized ammonia at times of low flow can be applied to the observed percent un-ionized ammonia for each month as a means of obtaining the critical value for percent un-ionized ammonia. This procedure could be used even if low flow is associated with low percent un-ionized ammonia, as it is for three of the 12 stations in this study. Alternatively, the test of association might show no significant association, in which case the procedure would be identical to the default procedure involving no association between the two variables.

If no site-specific information is available or if site-specific information is inadequate, a default computation is necessary. There are two simple options for default computation, as shown in Figure 2. The first of these is the assumption of perfect association between extreme low flows and extreme values of percent un-ionized ammonia. This is the assumption under which permits are currently prepared; it is the most conservative possible assumption concerning the relationship between low flow and un-ionized ammonia.

On strictly statistical grounds, based on the information from Colorado, the most logical choice would be the assumption of no significant association between low flow and percent un-ionized ammonia. In this instance, the calculation would be most accurate if the 50th percentile value of percent un-ionized ammonia is used for each month. However, an element of conservatism may be appropriate because the median will be exceeded half the time in a random sample. Therefore, a possible alternative is the 95th percentile or the mean plus two standard deviations for distributions that approach normality.

One additional possibility is not covered in Figure 2. If a parametric association could be detected between flow and percent un-ionized ammonia, particularly in the upper percentile range, it would be possible to calculate by parametric methods the percentile value of un-ionized ammonia corresponding to any specific value for low flow. Under these conditions, the DFLOW value could be used in estimating a corresponding value for percent un-ionized ammonia by use of an equation for the relationship between the two variables. This is not possible for the Colorado stations because no parametric relationships could be detected.

Conditions in other states might differ from those observed in Colorado. One strong feature of the data set for Colorado is the tremendous breadth of possibilities for months in which critical low flows and critical water quality conditions can occur. This may in turn be traced to the extensive manipulation of flow in Colorado, although a few stations in the 12-station data set are subject to only minor hydrologic manipulation. In states that show less extensive water diversion, some clearer associations may be established between extremes of water quality and extremes of flow.

Persistent use of the assumption that the most adverse conditions of flow coincide exactly with the most adverse conditions of water quality seems inadvisable for Colorado and possibly for other western states that have similar hydrologic regimes. Unless justified by site-specific characteristics, such practice will lead to excessively stringent requirements for removal of ammonia. Other priorities for water quality improvement may be higher.

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