IMPROVEMENTS IN THE COLORADO AMMONIA MODEL BY SIMULTANEOUS COMPUTATION OF EXTREMES IN FLOW AND WATER CHEMISTRY

by

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Abstract

The quantity of unionized ammonia in surface waters of the United States is regulated because unionized ammonia is toxic to aquatic life at relatively low concentrations (USEPA 1984). Regulation is achieved primarily through NPDES permit limitations on the total ammonia content (including both ionized and unionized fractions) of point source discharges. In Colorado, ammonia limits are established by the Colorado Water Quality Control Commission and are administered by the Colorado Department of Health Water Quality Control Division. The calculation of a permit limit for total ammonia requires simultaneous consideration of (1) critical low flows in the receiving water, and (2) critical values for the proportion of total ammonia that is unionized. Ionization of total ammonia is strongly affected by both pH and temperature. In preparing permits, it is standard practice both in Colorado and nationally to assume that critical conditions of low flow will coincide with conditions of pH and temperature that maximize the fraction of ammonia that is unionized. However, the true degree of association for extremes of flow, pH, and temperature has not been tested empirically. The present study reports the results of an analysis of association for extremes in pH, temperature, and low flow at 12 sites in Colorado for which an extensive data record is available (21 years at 12 or more samples per year). Statistical study of data for these sites showed no general relationship between flow and percent unionized ammonia at any station. Within periods of low flow, there was no parametric association between percent unionized ammonia and low flow. A nonparametric test of association between percent unionized ammonia and low flows showed that 8 of the stations have a random association of the two variables, i.e., the expected value of percent unionized ammonia during a period of low flow is equal to the mean value rather than an extreme value. At four of the stations, the association of low flow with percent unionized ammonia was nonrandom. Three of these showed a negative association, i.e., the percent unionized ammonia was significantly lower than the mean during periods of low flow. At a single station (the South Platte River near Kersey), there was a significant positive association, albeit a rather loose one, between percent unionized ammonia and extreme low flows; the lowest 5th percentile of low-flow values showed a mean of 77th percentile unionized ammonia. These findings suggest modifications of models that are used in computing maximum total ammonia for permits. The assumption of strong association between the least favorable flows (low flow) and least favorable percent unionized ammonia (high percent unionized ammonia) is not justified by field information and may result in overly stringent ammonia control requirements for point source discharges.

Introduction

The amount of ammonia that can be discharged to surface waters from a point source in Colorado is regulated by an NPDES permit that is issued by the State in compliance with the Clean Water Act. In preparing permits, the Colorado Department of Health Water Quality Control Division, under review by USEPA Region VIII, employs historical information on discharge and stream chemistry at the point of wastewater discharge for any given permit. Even when extensive information is available on flow and water chemistry, the computation of allowable maximum discharge for total ammonia is complicated by a variety of factors including dilution, mixed temperature and pH at the point of discharge; decay of total ammonia below the point of discharge as a result of biological conversion; changes of pH and temperature below the point of discharge; 24-h and 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 and the partitioning between ionized ammonia and unionized ammonia, given that unionized ammonia is the direct basis for water quality standards. A model that is being used for this purpose in Colorado is designated the Colorado Ammonia Model (CAM, Saunders et al. 1991). This model was prepared by the Center for Limnology at the University of Colorado, Boulder, specifically for use with Colorado's water quality standards for ammonia. The model takes into account a wide variety of factors that affect the concentration of unionized ammonia in streams at or below the point of discharge. Special features of the model that previously were difficult or impossible to account for in the preparation of discharge permits include: (1) rebound of pH and temperature below the point of mixing, (2) 24-h cycling of temperature and pH, (3) use of quantitative methods to select critical combinations of pH and temperature, and (4) reasonable estimates for daily or seasonal oscillations in pH and temperature when empirical information is not available. In addition, the model incorporates pH and temperature at the point of discharge, degree of dilution, nitrification below the point of discharge, and background ammonia concentrations at the point of discharge.

A model similar to the Colorado Ammonia Model has been prepared by the University of Colorado Center for Limnology for use by USEPA Region VIII (Saunders et al. 1992). This model, which is called AMMTOX, is similar to the Colorado Ammonia Model except that it has a more generalized basis reflecting the national criteria that are used by the USEPA in evaluating water quality standards of individual states.

Any model that can be used in calculating the maximum allowable total ammonia concentration for a point-source effluent will require some assumption about the correlation between water quality and flow. 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 the critical low flow in the receiving water, i.e., the condition of least dilution. In the State of Colorado, and for the USEPA, the critical low flow is the biologically-based low flow (DFLOW) as defined by the USEPA (Rossman 1990). Other states may use hydrologically-based low flows such as the 7Q10, 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 unionized. The percent of total ammonia that is unionized increases directly in response to increase in pH and increase in temperature (Emerson et al. 1975). The regulatory authority sets critical concentrations for unionized ammonia and specifies a critical probability of exceedence for these concentrations. (In Colorado 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 for a given month can be calculated, as they are in CAM or AMMTOX, 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 for each month. These combinations, with their corresponding values for percent unionized 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 critical combinations of pH and temperature is that the critical 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 randomly associated 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 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 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 conditions for pH and temperature and critical conditions for flow. The report is designed to establish a foundation for adding a new level of realism to the CAM and AMMTOX 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 is an interesting one with wide implications.

Design and Methods of the Study

The design of the study is empirical, i.e., it 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 this 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 appropriate water quality variables (in this case, temperature and pH). Within the State of Colorado, 12 stations satisfied these criteria (Figure 1). The stations are listed in Table 1 along with some of their characteristics.

Hydrologic records were assembled for each of the 12 stations. Data for each station were processed with the USEPA's DFLOW algorithm to produce the biologically-based low flow estimates for 1-d 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 on a weekly, biweekly, or monthly basis. The total number of water quality measurements for each station is given in Table 1. The flow corresponding to each water quality measurement was established for each station by using the hydrologic data base.

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, pH, and temperature. The main focus of the analysis is on extremes of low flow and their association with extreme values of pH and temperature. Extreme values of pH and temperature for present purposes are those that result in highest values for percent unionized ammonia.

Results

Discharge

Figure 2 shows the frequency distribution of discharge for each of the 12 stations. As expected, all of the distributions show strong positive skew when plotted on an arithmetic scale (i.e., the discharge tends to be log-normally distributed). Mean discharges vary from 2633 cfs for the Gunnison River southeast of Grand Junction to 76 cfs for Boulder Creek at County Line Road. The stations are widely distributed over the State, represented a variety of elevations, and reflect varying degrees of hydrographic control through diversion (Table 1).

Table 2 gives the low-flow (DFLOW) values for each of the stations and shows the number of days, month by month, for which the flow was equal to or less than the low flow. It is clear from the table that the stations include a variety of hydrologic regimes that reflect variations in location and patterns of diversion. The table shows that the 12 streams collectively have critical flows in all 12 months of the year. Most streams show critical low flows in more than one season. The highest frequency of low flows among all 12 streams is for the spring months (March, April, May) and for August. The lowest incidence of low flows is in June and July and in January and February. Overall, Table 2 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. As shown by Table 3 and Figure 3, 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. 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.

Water Quality

The water quality variable of direct concern in computing the total ammonia allowance for a stream is the percent unionized ammonia, which is under direct control of pH and temperature. For each sampling date at each station, the pH and temperature information was used in calculating a percent unionized ammonia. The distribution of these values as a function of flow is shown in Figure 4. The plots show a wide range in the number of extreme values, reflecting contrasts in the range of pH and temperature combinations across the 12 stations. The highest values for percent unionized ammonia are scattered across a wide range of discharges at all of the stations.

Table 4 gives the mean percent unionized ammonia at each of the stations, and also shows the distribution of most extreme values across months of the year for each station. Unionized ammonia in excess of 10% of total ammonia was taken as an arbitrary indicator of extreme values. As shown by Table 4, these extremes can be found at at least one of the sampling stations in any month of the year. However, the highest number of extreme values occurs in the warm months of the year. This reflects partly the influence of temperature on unionized 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, January, and

February show the smallest incidence of extreme values for percent unionized ammonia.

General Relationships Between Discharge and Percent Unionized Ammonia

The plots of percent unionized ammonia in relation to flow shown in Figure 4 do not suggest any general relationship between percent unionized ammonia and flow. This is confirmed by statistical analysis as summarized in Table 5. Following a log transformation to improve bivariate normality, the two variables show no significant relationship for any station.

The analysis of relationships between percent unionized ammonia and flow was repeated for individual months on grounds that relationships for individual months might be obscured if the months are combined. Only a few relationships are significant, and even these are relatively weak (Table 5).

Percent Unionized Ammonia at Times of High Flow

Two approaches were taken to the analysis of association between flow and percent unionized ammonia at times of low flow: (1) parametric regression analysis of the association between percent unionized ammonia and discharge under low-flow conditions, and (2) a nonparametric analysis of the association between percent unionized ammonia and low-flow conditions.

The regression analysis for each station was confined to those conditions under which flow was less than or equal to the 5th percentile flow. This resulted in the selection of 7 to 23 sampling dates for each station, depending on the frequency of water quality sampling for the station. For the selection of low-flow dates at each station, the corresponding percent unionized ammonia was obtained from the pH and temperature data. Percent unionized ammonia was then regressed against discharge. Table 6 summarizes the results. In no instance was there a significant association between discharge and percent unionized ammonia for dates showing discharges within the 5th percentile of discharge for the entire data record.

The second test of association between discharge and percent unionized ammonia also involves selection of dates on which the discharge was equal to or below the 5th percentile, and computation of the percent unionized ammonia for each of these dates at each station, as well as a cumulative percentile value for percent unionized ammonia on each date. The following hypothesis was then formulated for testing at each station: When the discharge is equal to or below the 5th percentile for the entire data record, the percentile rank for percent unionized 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 unionized ammonia will show up in terms of a percentile rank for unionized ammonia that is significantly above the 50th percentile. This hypothesis was tested nonparametrically by use of the chi-square statistic. For a given number of data records below the 5th percentile of flow, the expectation for random association is that half of the observed values for unionized ammonia will be above the 50th percentile and half will be below. The observed can be compared with this expectation by use of the chi-square statistic.

Table 6 summarizes the results of the chi-square test. Eight of the 12 stations show no significant deviation from a random association between low discharge and percent unionized ammonia. Four stations do show a statistically significant deviation (at $\alpha = .05$), but three of these associations are the inverse of the association postulated by the working hypothesis, i.e., the percentile rank of unionized 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 chi-square test was repeated for the composite of low-flow values at all stations. This test showed no association between low flow and percentile rank of unionized ammonia values (Table 6).

Discussion and Interpretation

The standard assumption for regulatory practice is that critical low flows are statistically associated with critical conditions for percent unionized 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 unionized 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 unionized ammonia opens several possibilities for preparation of NPDES permits. These possibilities are summarized in Figure 5. After the critical low-flow values and critical percent unionized 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 that, at least for Colorado, the more logical way to proceed would be through a decision tree such as is shown in Figure 5. The first branch in the decision tree 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 unionized ammonia and low flow is very 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 can be made on them. If a statistically significant association is present, the mean percentile value for unionized ammonia at times of low flow can be applied to the observed percent unionized ammonia for each month as a means of obtaining the critical value for percent unionized ammonia. This procedure could be used even if the association between low flow and percent unionized ammonia is negative, 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 a 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 5. The first of these is assumption of perfect association between extreme low flows and extreme values of percent unionized ammonia. This is the assumption under which all permits are currently prepared; it is the most conservative possible assumption concerning the relationship between low flow and unionized 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 unionized ammonia. In this instance, the calculation would be most accurate if the 50th percentile value of percent unionized 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 reasonable 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 5. If a parametric association could be detected between flow and percent unionized ammonia, particularly in the upper percentile range, it would be possible to calculate by parametric methods the percentile value of unionized 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 unionized 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 (Table 1). 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 unionized ammonia. Other priorities for water quality improvement may be higher.

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USGS Station Number	Drainage Area, mi^2	Elevation, ft	Remarks	Hydrologic Influences	Number of water quality samples
Arkansas River near Nepesta, #7117000	9345	4385	records fair except estimated daily discharges are poor	transmountain diversion, storage reservoir, power development, irrigation diversion (230,000 acres), irrigation return flow, flow regulated by Pueblo Reservoir since 1-9-74.	366
South Platte River near Kersey, #6754000	9598	4576	records fair	transmountain diversion, storage reservoir, power development, ground-water withdrawal, irrigation diversion (888,000 acres), irrigation return flow	418
South Platte River at Henderson, #6720500	4713	5003	records good, no estimated discharges	transmountain diversion, storage reservoir, ground-water withdrawal, irrigation diversion (253,000 acres), irrigation return flow	422
Cache la Poudre River near Greeley, #6752500	1877	4610	records good except estimated daily discharges, which are fair	transmountain diversion, transbasin diversion, storage reservoir, power development, municipal water supply, irrigation diversion (250,000 acres), irrigation return flow	411
*Big Thompson River near mouth, #6744000	828	4680	records good	transmountain diversion, storage reservoir, power development, irrigation diversion (95,000 acres), irrigation return flow	412

Table 1 (beginning)

USGS Station Number	Drainage Area, mi^2	Elevation, ft	Remarks	Hydrologic Influences	Number of water quality samples
Boulder Creek at Boulder/Weld county line, #6727000	102	5826	records good except estimated daily discharges are fair	flow regulation by Barker Reservoir (capacity: 11,500 acre-ft), low flow during non-irrigation season regulated by Orodell power plant (1,500 ft. upstream)	417
*Clear Creek near mouth, #6720000	575	5110	records good	transmountain diversion, storage reservoir, irrigation diversion (75,000 acres), irrigation return flow	260
Colorado River near Dotsero #9070500	4394	6130	records good except estimated daily discharges are poor	transmountain diversion, storage reservoir, irrigation diversion (68,000 acres), irrigation return flow	315
Eagle River at Gypsum, #9070000	945	6275	records good, no estimated daily discharges	transmountain diversion, transbasin diversion from Robinson Reservoir (2520 acre-ft capacity) to Tenmile Creek for mining development, many small diversions for hay meadows.	134
Roaring Fork River at mouth, #9085000	1451	5721	records good except estimated daily discharges are fair	transmountain diversion to Arkansas River, storage reservoir (Ruedi Reservoir, since May 1968), irrigation diversion (35,000 acres	132
Gunnison River southeast of Grand Junction, #9152500	7,928	4628	records good except estimated daily discharges are fair	storage reservoir, irrigation diversion (233,000 acres), irrigation return flow	147

Table 1 (continued)

USGS Station Number	Drainage Area, mi²	Elevation, ft	Remarks	Hydrologic Influences	Number of water quality samples
Uncompahgre River at Delta, #9149500	1115	4926	records good	transbasin diversion, irrigation diversion 90,000 acres), irrigation return flow	260

*Information from *Water Resources Data for Colorado Water Year 1975*. All other entries from *Water Year 1990*.

Table 1 (concluded). Description of the 12 sampling stations that were used in the study.

USGS Station	DFLOW, cfs		Days Below 1-d Biologically-based Low Flow												
	acute	chronic	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
Clear Creek near mouth	0.7	2.7				2	2							3	7
South Platte River at Henderson	63.8	132.1		3	6										9
Boulder Creek at county line	2.0	5.0	2									3		1	6
Big Thompson River near mouth	1.4	10.2				4		1							5
Cache la Poudre River near Greeley	6.8	15.1					3								3
South Platte River near Kersey	69.9	144.8				8	7								15
Arkansas River near Nepesta	43.9	91.7								1			6		7
Eagle River at Gypsum	106.8	140.1		1						3	8		1		13
Colorado River near Dotsero	545.6	665.7	1	1	1								1	3	7
Roaring Fork at mouth	275.0	335.9			1	1				8					10
Uncompahgre River at Delta	50.9	83.8			8	4									12
Gunnison River southeast of Grand Junction	460.4	585.8				4			4	7					15
Monthly Totals			3	5	16	23	12	1	4	19	8	3	8	7	109

Table 2. Number of days in the entire 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 at each of the 12 stations used in the study. In addition, the value of the biologically-based low flow at each station is shown.

Month	R^2	b	Standard Error b	a	Standard Error a	N
Minimum log 30-d vs. log 1-d						
April	0.98	0.82	0.04	0.54	0.13	12
August	0.99	0.94	0.02	0.25	0.06	12
September	0.99	0.87	0.02	0.38	0.06	12
December	0.98	0.85	0.04	0.41	0.13	12
DFLOW, 30-d vs. mean flow						
	0.90	0.26	0.03	-30.5	73.3	12
DFLOW, 1-d vs. mean flow						
	0.86	0.21	0.03	-38.4	73.8	12

Table 3. Relationship of the minimum 30-d mean flow (transformed logarithmically) to the minimum 1-d flow (transformed logarithmically) given as y = bx + a, where y = the logarithm of the 30-d minimum (cfs) and x = the logarithm of the 1-d minimum (cfs).

USGS Station Number	Mean Percent Unionized	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Site Totals
Clear Creek near mouth	4.1			1	4	1		4	7	4	7			28
South Platte River at Henderson	1.2						1		1					2
Boulder Creek at county line	6.9		1	2	10	11	8	14	17	15	5	1	1	85
Big Thompson River near mouth	2.6		1		2	1	1	1	2					8
Cache la Poudre River near Greeley	2.0				2	1	1	1	1					6
South Platte River near Kersey	2.2			1				2	1				1	5
Arkansas River near Nepesta	2.8				1	2	2		1	2		1		9
Eagle River at Gypsum	4.5							4	2	3				9
Colorado River near Dotsero	3.7						1	3	6	6	1			17
Roaring Fork at mouth	5.3	1	2	4	1		3	1	3	2		1		18
Uncompahgre River at Delta	3.2		1	1		1			1	2				6
Gunnison River southeast of Grand Junction	5.7			1	2		1	5	3	2	2	1		17
Monthly Totals		1	5	10	22	17	18	35	45	36	15	4	2	210

Table 4. Distribution of extreme values for percent unionized ammonia (values above 10%) across months for each of the 12 stations used in the study. In addition, the mean percent unionized ammonia at each station is shown.

Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Clear Creek near mouth	0.04	0.08	0.14	0.10	0.06	0.07	0.13	0.15	0.00	0.05	0.00	0.06
South Platte River at Henderson	0.01	0.01	0.04	0.07	0.05	0.01	0.05	0.08	0.05	0.02	0.06	0.02
Boulder Creek at county line	0.00	0.00	0.10	0.14*	0.03	0.01	0.16*	0.00	0.01	0.01	0.04	0.05
Big Thompson River near mouth	0.02	0.01	0.08	0.00	0.06	0.00	0.02	0.00	0.00	0.06	0.07	0.05
Cache la Poudre River near Greeley	0.24*	0.01	0.02	0.03	0.04	0.04	0.00	0.00	0.01	0.01	0.04	0.00
South Platte River near Kersey	0.00	0.02	0.02	0.08	0.21*	0.20*	0.00	0.03	0.00	0.06	0.01	0.02
Arkansas River near Nepesta	0.19*	0.29*	0.03	0.04	0.06	0.01	0.00	0.09	0.07	0.10	0.03	0.01
Eagle River at Gypsum	0.06	0.14	0.05	0.00	0.27	0.15	0.12	0.05	0.03	0.13	0.15	0.37
Colorado River near Dotsero	0.01	0.01	0.01	0.09	0.19*	0.23*	0.07	0.17*	0.02	0.02	0.02	0.03
Roaring Fork at mouth	0.00	0.72*	0.26	0.26	0.24	0.21	0.05	0.06	0.04	0.01	0.00	0.04
Uncompahgre River at Delta	0.00	0.00	0.13	0.00	0.21*	0.16*	0.17	0.05	0.00	0.03	0.03	0.18
Gunnison River southeast of Grand Junction	0.23	0.04	0.37	0.43*	0.47*	0.13	0.00	0.62*	0.00	0.01	0.08	0.22

Table 5. A summary of the statistical tests for relationships between percent unionized ammonia and discharge (untransformed). The values shown in the table are for r^2. Values representing relationships that are significant (α = .05) are indicated with an asterisk.

Station Name	Mean % un-ionized	Stan-dard Devi-ation	Mean dis-charge, cfs	Stan-dard Devi-ation	N	R^2	Chi square
Clear Creek near mouth	8.1	11	2.6	0.8	17	0.00	3.8
South Platte River at Henderson	0.9	0.6	141.5	23.5	23	0.45	0.2
Boulder Creek at county line	3.8	5.9	5.4	1.4	13	0.28	1.0
Big Thompson River near mouth	4.2	1.7	16.4	7.7	20	0.01	8.1*
Cache la Poudre River near Greeley	2.3	1.7	14.5	3.7	21	0.01	2.9
South Platte River near Kersey	4.3	2.9	150.5	36.3	23	0.02	9.6*
Arkansas River near Nepesta	3.7	4.9	96.5	22.3	22	0.00	2.3
Eagle River at Gypsum	4.0	4.6	143.1	4.7	7	0.28	3.5
Colorado River near Dotsero	1.5	0.8	690.2	35.4	20	0.03	8.1*
Roaring Fork at mouth	6.6	5.6	339.3	34.1	10	0.21	0.0
Uncompahgre River at Delta	3.3	3.1	85.8	10.6	13	0.05	6.5*
Gunnison River southeast of Grand Junction	7.6	2.4	601.8	77.5	13	0.09	3.1
All stations							

*Association is significant at $\alpha = 0.05$

Table 6. A summary of the statistical tests for associations between percent unionized ammonia and discharge at low discharges (discharges below the 5th percentile). The mean percentile for percent unionized ammonia is shown in the first column, followed by its standard deviation. Mean discharge for values less than or equal to the 5th percentile is also shown along with its standard deviation, as is the number of points falling below the 5th percentile for discharge. R^2 indicates the result of a regression analysis of the two variables, and the chi-square value indicates the result of a test of association between percentile values for dates falling within the 5th percentile for discharge.

Table Captions

Table 1. Description of the 12 sampling stations that were used in the study.

Table 2. Number of days in the entire 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 at each of the 12 stations used in the study. In addition, the value of the biologically-based low flow at each station is shown.

Table 3. Relationship of the minimum 30-d mean flow (transformed logarithmically) to the minimum 1-d flow (transformed logarithmically) given as $y = bx + a$, where y = the logarithm of the 30-d minimum (cfs) and x = the logarithm of the 1-d minimum (cfs).

Table 4. Distribution of extreme values for percent unionized ammonia (values above 10%) across months for each of the 12 stations used in the study. In addition, the mean percent unionized ammonia at each station is shown.

Table 5. A summary of the statistical tests for relationships between percent unionized ammonia and discharge (untransformed). The values shown in the table are for r^2. Values representing relationships that are significant ($\alpha = .05$) are indicated with an asterisk.

Table 6. A summary of the statistical tests for associations between percent unionized ammonia and discharge at low discharges (discharges below the 5th percentile). The mean percentile for percent unionized ammonia is shown in the first column, followed by its standard deviation. Mean discharge for values less than or equal to the 5th percentile is also

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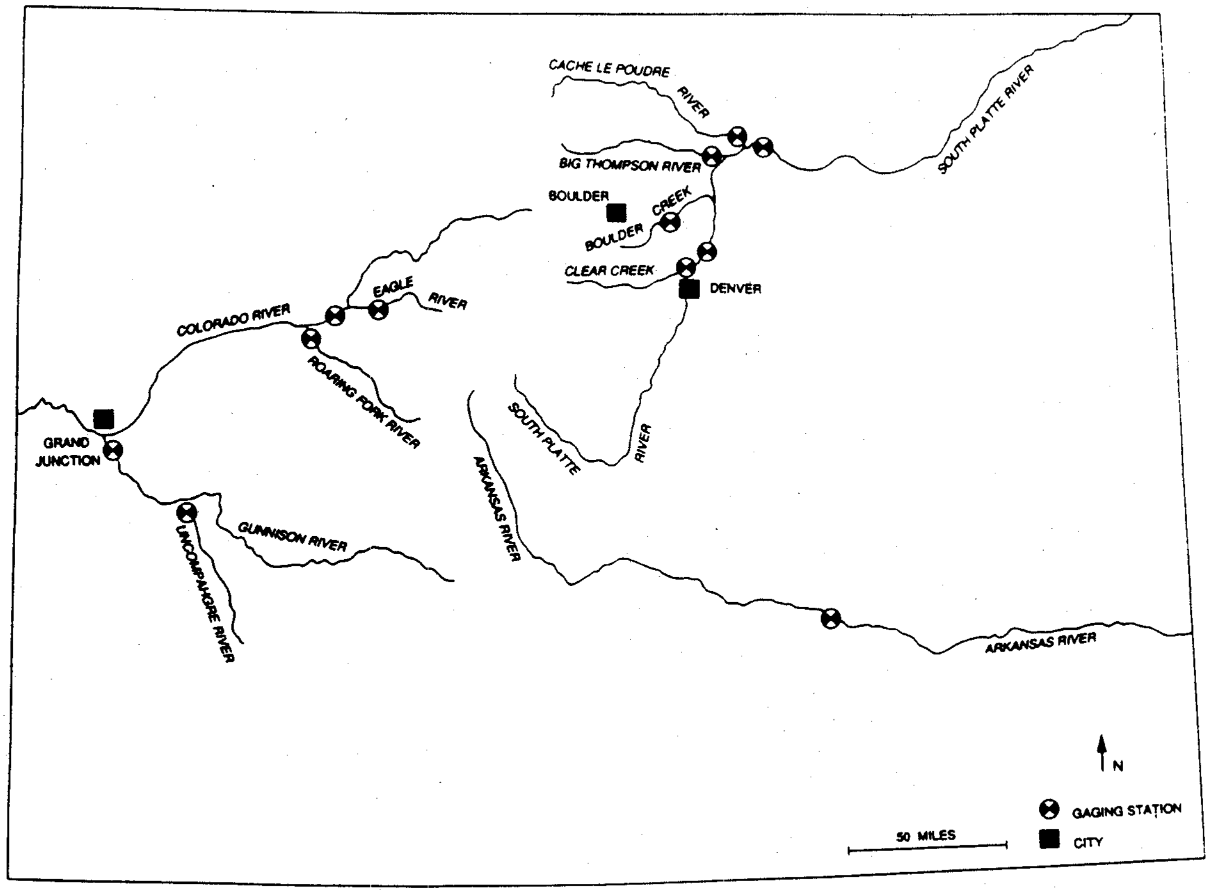

Figure 1. A map of the State of Colorado showing the approximate location of the 12 stations that were used in the study.

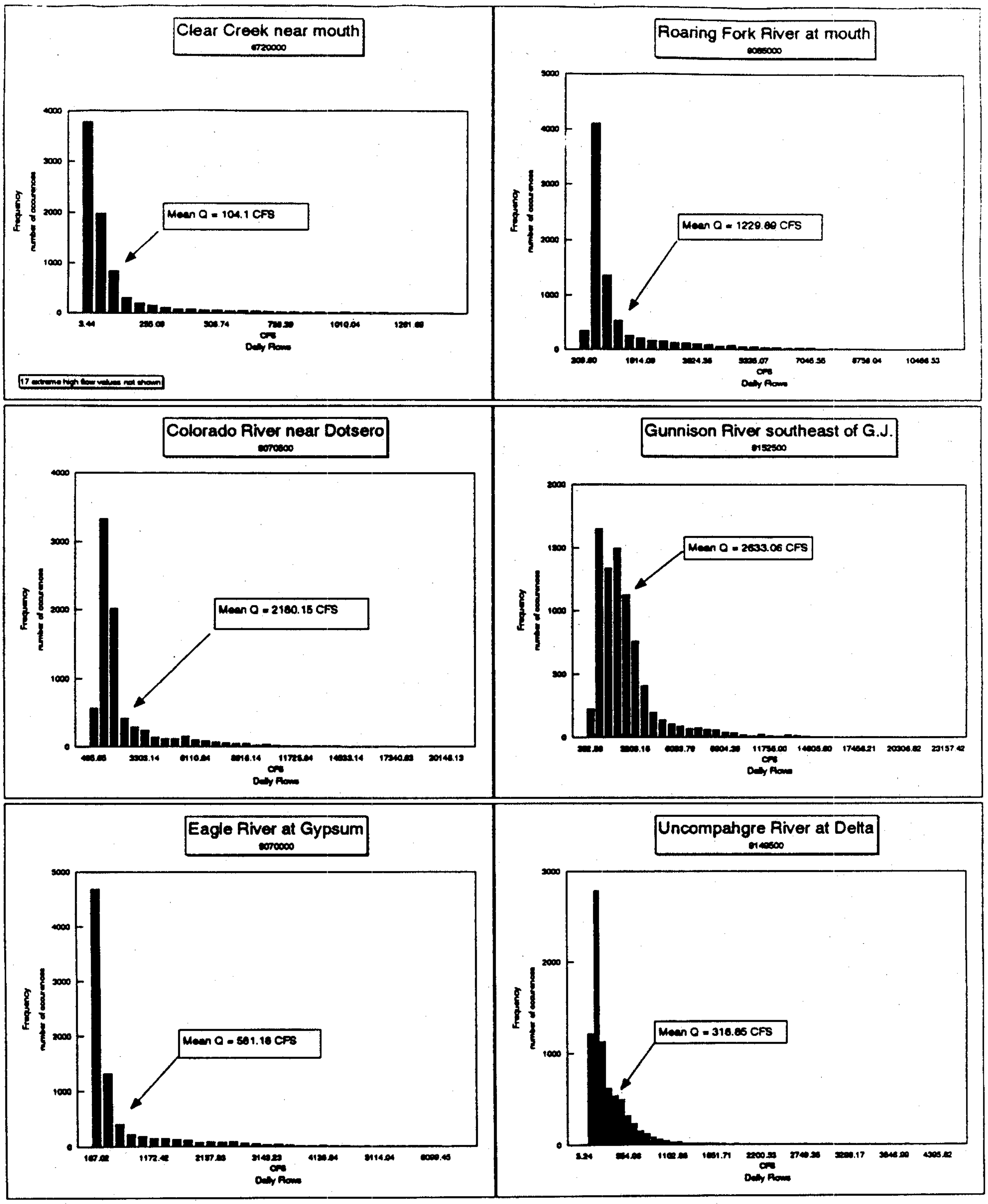

Figure 2. Frequency distributions of flow for the 12 stations that were used in the study.

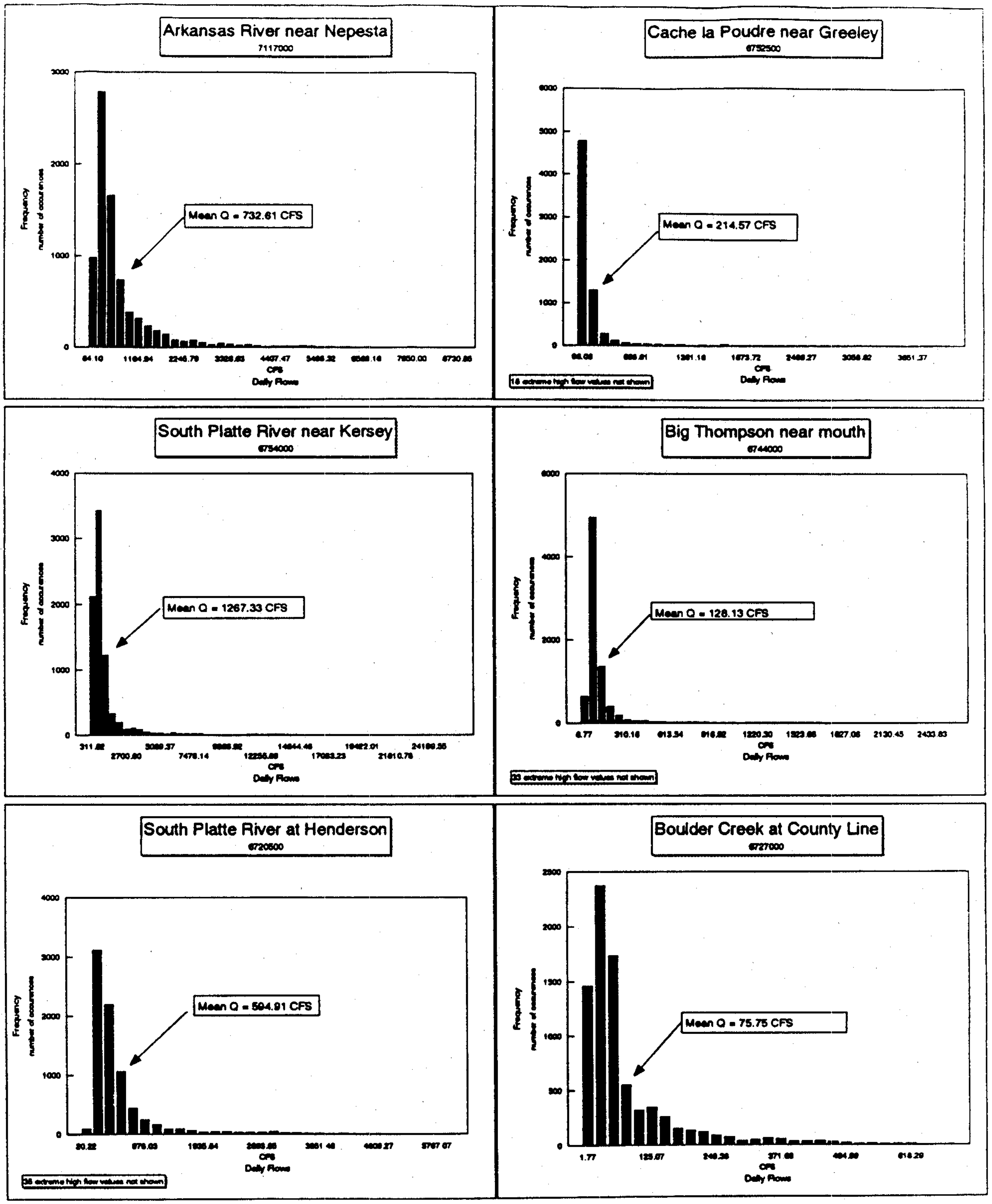

Figure 2, part 2.

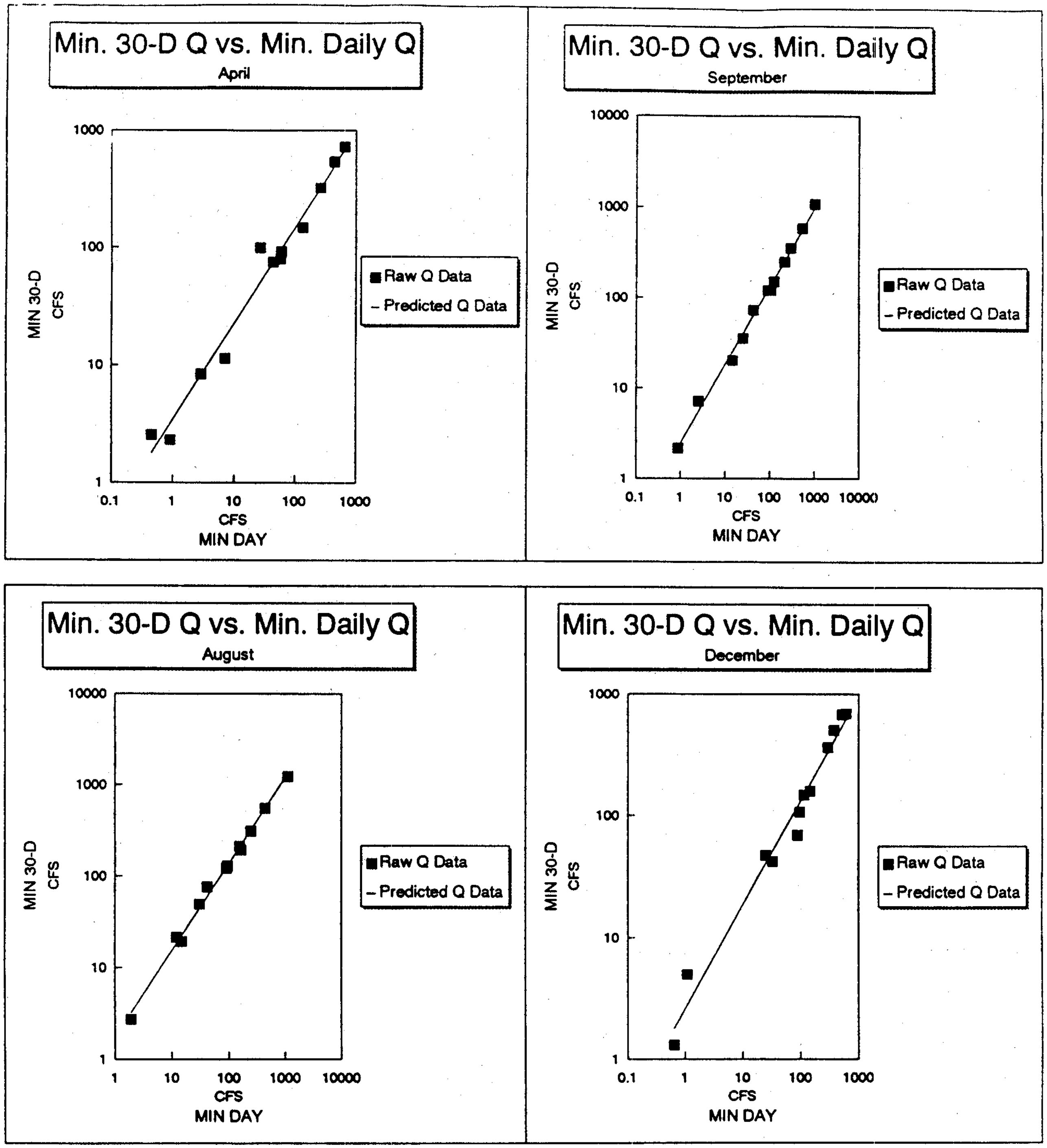

Figure 3. Scatter plots of critical low-flow values for 1-d averaging period vs. values for 30-d averaging periods across the 12 stations included in the study for 4 months of the year.

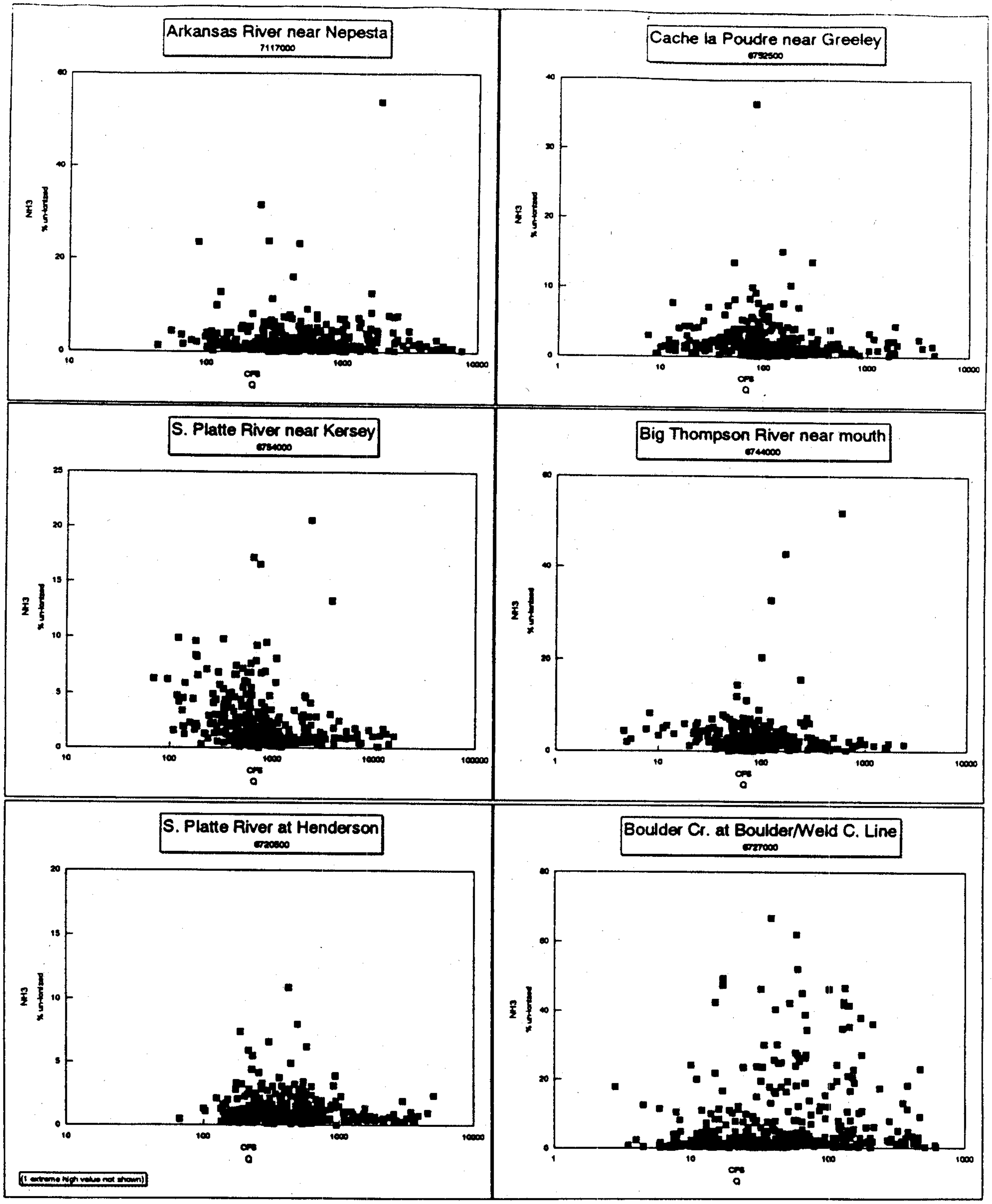

Figure 4. Plots of the relationship between percent unionized ammonia and discharge.

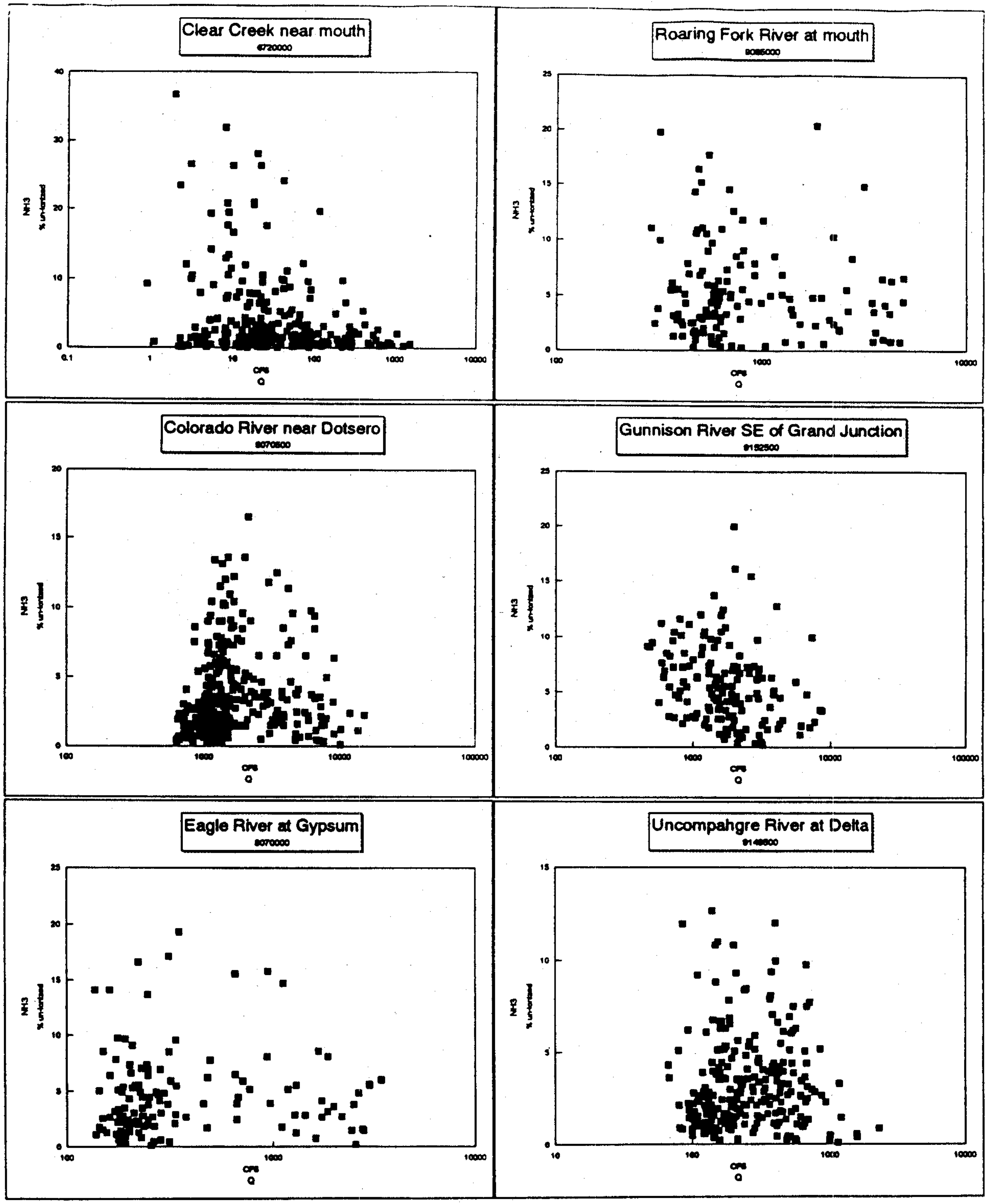

Figure 4, part 2.

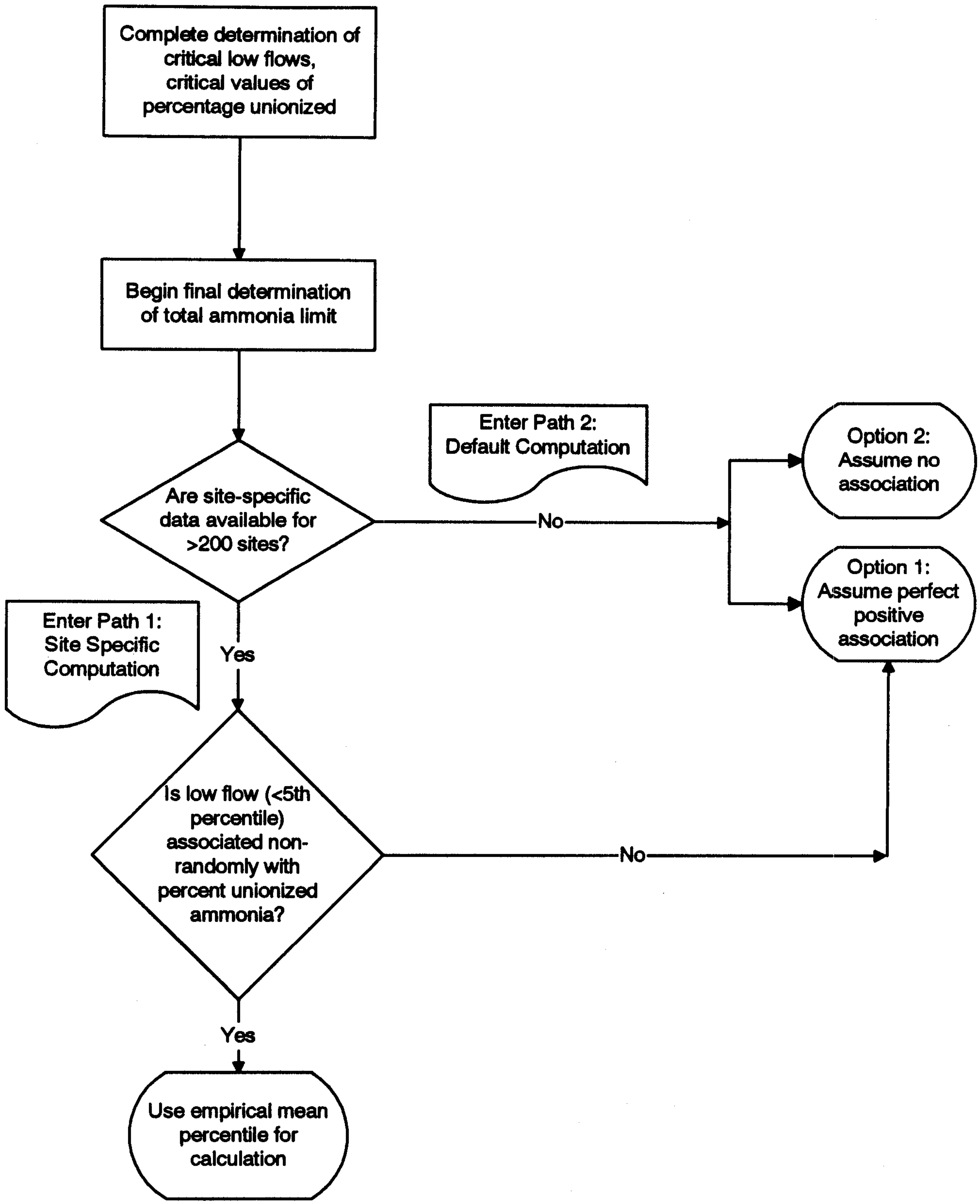

Figure 5. Decision diagram for treatment of the relationship between low flow and percent unionized ammonia.

Figure Captions

Figure 1. A map of the State of Colorado showing the approximate locations of the 12 stations that were used in the study.

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