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Use of the Hazard Assessment Approach for Evaluating the Impact of Chlorine and Ammonia in Pueblo, Colorado, Domestic Wastewaters on Water Quality in the Arkansas River

REFERENCE: Lee[1], G. Fred, Jones, R. A., Newbry, B. W., and Heinemann. T. J., "Use of the Hazard Assessment Approach for Evaluating the Impact of Chlorine and Ammonia in Pueblo, Colorado, Domestic Wastewaters on Water Quality in the Arkansas River," *Aquatic Toxicology and Hazard Assessment: Fifth Conference ASTM STP 766, J. G.* Pearson, R. B. Foster, and W. E. Bishop, Eds., American Society for Testing and Materials, 1982, pp. 356-380.

ABSTRACT: A short-term. intensive study has been conducted on the potential impact of the chlorine, and to a lesser extent the ammonia and nitrite, associated with the domestic wastewater discharge from the city of Pueblo, Colo. on the water quality (beneficial uses) of the Arkansas River downstream from the discharge. The hazard assessment approach was used in the planning of the study and in data interpretation.

The wastewater treatment plant (WWTP) effluent mixed slowly with the river, forming a narrow effluent plume extending downstream for about 1000 m; in this "zone of mixing" contaminant concentrations were sufficient to kill caged fathead minnows in 4 days or less. A continuous "zone of passage" existed past the discharge in which no visually apparent adverse effects on caged fish were found in 4 days exposure.

Chlorine concentration decreased with the distance downstream of the discharge, but, based on the concentrations found, there is a potential for chlorine impact on aquatic life for a distance of about 15 km. Outside the zone of physical mixing of the effluent and the river, nitrite and un-ionized ammonia concentrations were below the corresponding Colorado water quality guidelines; however, questions regarding their impact on the water quality within this zone were raised and need to be addressed in future studies.

KEY WORDS: domestic wastewater, chlorine, ammonia, nitrite, hazard assessment, water quality, aquatic toxicology

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The city of Pueblo, Colo., like many other cities in the United States, is facing expansion of its domestic wastewater treatment plant (WWTP) to meet the demands of a growing population. At the same time, the Colorado Water Quality Control Commission is in the midst of its hearings for use-classification of Colorado rivers, including the Arkansas River, which receives the city of Pueblo's domestic wastewater discharges. The results of these hearings will establish not only the beneficial uses to be protected of the reach of the river considered but also the numerical water quality standards applicable to it. Of particular concern to the city of Pueblo are the numerical standards for chlorine, ammonia, and nitrite that the commission assigns to the Arkansas River below its discharge, since these standards may necessitate the removal of these chemicals prior to effluent discharge. That would require advanced wastewater treatment not normally achieved during secondary treatment of municipal wastewaters. Because of the substantial financial investment that would have to be made in a new facility (or an existing one) to remove these chemicals, it is appropriate to determine what improvements in water quality in the Arkansas River would be likely to result from reducing the loads of these contaminants from the Pueblo WWTP effluent. Although Pueblo is currently practicing partial dechlorination, it is important to evaluate whether or not this additional treatment needs to be done or included in expanded facilities in order to protect the desired beneficial uses of the river below the discharge.

Part of the concern with regard to the standards to be set and the removal of WWTP effluent contaminants is the fact that, in the past, the water quality "guidelines" developed in Colorado have been in large part equivalent to concentrations which will not have an impact on sensitive aquatic organisms when they receive chronic, life-time exposure to that concentration or which are based on other "worst-case" situations. There are several factors, however, which render the direct use of such guidelines as concentration limits inappropriate in most natural waters. Among these are the facts that the concentrations of contaminants, especially those from a WWTP effluent, in natural waters are rarely constant; it is likely that many organisms of concern in this situation would not receive a life-time exposure to concentrations in excess of chronic safe levels; and factors other than the composition of the water can dictate what organisms can exist therein (such as habitat). It is important, therefore, that the potential impact of a contaminant on water quality (that is, on beneficial uses of the water) be evaluated on a site-specific basis before funds are spent to control existing or proposed contaminant discharges.

Over the past year and a half the authors of this paper have been conducting a series of studies on the persistence and potential impact of chlorine, ammonia (NH_3), and nitrite derived from the domestic wastewater discharges of a number of Colorado Front Range communities (that is, those communities at the eastern base of the Colorado

Rocky Mountain foothills). As part of these studies, in early March 1980 an investigation was made of the persistence in the Arkansas River of chlorine and, to a lesser extent, ammonia and nitrite from the Pueblo WWTP. The investigation was focused primarily on chlorine behavior within the zone of physical mixing of the discharge with the river, but it included an evaluation of the behavior of these chemicals outside that area as well. The studies were designed and the results were interpreted using a hazard assessment approach.

The Hazard Assessment Approach

Water quality, as classically defined and as used in assessing the impact of a contaminant, must be viewed and evaluated in relation to the desired beneficial uses of a particular body of water; what is good water quality for a fishery may not be good water quality for aesthetic enjoyment of the water body. Acceptable or desirable water quality is, thus, a social assessment. The *hazard assessment approach* is a selective, sequential testing-evaluation scheme which produces information that can be used to estimate the impact on a given use of controlling the input of a given contaminant or discharge. Two basic types of information are sought: (1) the aquatic chemistry of the contaminant or contaminants (their rates of transformation, environmental concentrations, and patterns of distribution) and (2) the aquatic toxicology of the contaminant or contaminants, which in general defines the expected impact on aquatic organisms of a given duration or pattern of exposure to a given concentration or concentrations. These two bodies of information are evaluated to determine the impact of a given level of discharge or expected change in discharge on aquatic organisms (or other characteristics of the water depending on the concern) under a given set of environmental circumstances, such as for a particular river reach.

In order for hazard assessment studies to be as cost-effective as possible, they should be conducted under worst-case conditions. Generally, worst-case conditions in a river system would be characterized by low flow and the presence of maximum concentrations of contaminant forms which could impair beneficial uses of the river. For the contaminants of major concern in this study (chlorine and ammonia), there are two periods of the year when investigations should be conducted: the winter low flow and summer low flow. The winter low-flow studies would be expected to show the greatest persistence of these chemicals; during the summer low-flow periods the highest percentage of total ammonia in the un-ionized form would exist because of elevated temperatures and pH values.

The results of the hazard assessment are used, along with habitat characteristics, economic considerations, and desires of the public for water use, to make decisions regarding the degree of contaminant control desired. Details of the approach and its development have been discussed by Cairns et al. [1], Dickson et al. [2], and Lee et al. [3], and details of its application to domestic wastewater discharges have been presented by Lee et al. [4].

Description of the Arkansas River Study Area

The study area of the Arkansas River is shown in various degrees of detail in Fig. 1. The Pueblo WWTP is a trickling filter facility which, at the time of the study (6 to 11 March 1980), was discharging 0.22 to 0.7 m^3/s (5 to 16 million gal/day). The plant discharge flows down a relatively steep, approximately 200-m side channel before entering the Arkansas River at a point about 1.8 km downstream of its confluence with Fountain Creek and about 1.7 km upstream from the CF & I steel mill wastewater discharge. The river in the vicinity of the Pueblo WWTP was about 30 m wide and about 0.3 to 1 m deep. Its flow, which is largely regulated by an upstream dam, was a fairly constant 4.8 m^3/s during the study, which was only slightly greater than the recent-year winter low flow. The water temperatures during the study were generally between 2 and 14ºC with diel fluctuations of about 10 deg Celsius. The conditions of the river at the time of the study were essentially worst-case for winter. While funds were not available to conduct a companion study under summer worst-case conditions, an inference can be drawn about the persistence of these contaminants under those conditions from the results of other studies on the Arkansas River near Pueblo and of studies conducted by the authors on the persistence of chlorine and ammonia in other Colorado Front Range streams.

The riverbed consisted of coarse sand which formed dunes or sand waves that progressively moved through the study area. Some warmwater game fish have been found below the Pueblo WWTP discharge, although their numbers have been few; they appear to have been fugitives from upstream sources. While superficially it might be thought that a good warmwater sports fishery could be developed below the Pueblo WWTP discharge, there are a number of factors which greatly inhibit this development, the most important of which is the high sediment load discharged to the Arkansas River by Fountain Creek just above the point at which the Pueblo WWTP discharge occurs. This changes the riverbed characteristics in comparison with those upstream, thus reducing the numbers and types of fish food organisms, as well as the desirable fish. There is no public access to the river in the study area except at highway bridges, the first of which is about 15 km downstream from the WWTP.

[4] The italic numbers in brackets refer to the list of references appended to this paper.

Colorado

Colorado Springs

Study Area

Pueblo County

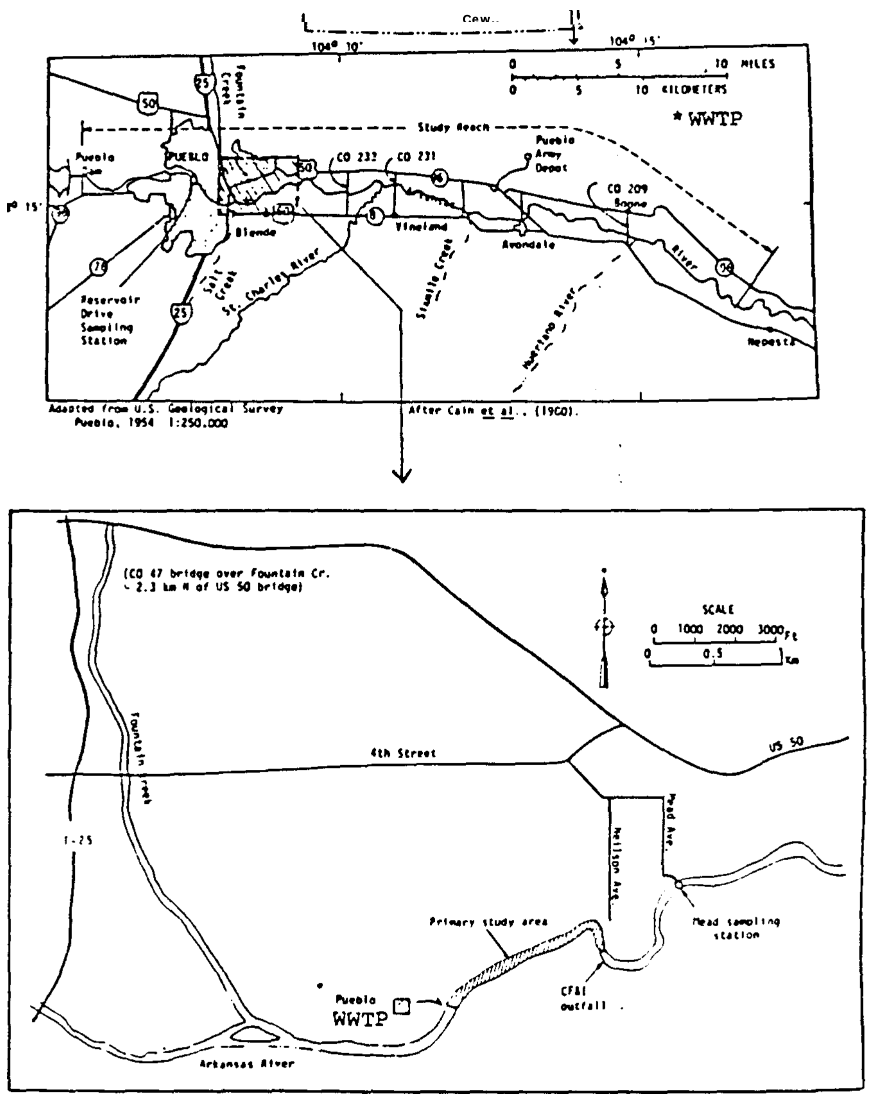

FIG. *1—Location of the study area (after Lee et a1 [5]).*

Methodology

There were two major components of the Arkansas River study: (1) the determination of the concentrations of chlorine, nitrite, and ammonia, as well as other selected parameters in the WWTP discharge and both upstream and downstream thereof; and (2) the evaluation of the toxicity of the effluent to caged fish placed at selected locations in relation to the discharge, as shown in Fig. 2. Lee et al. [5,6] present a detailed discussion of the analytical techniques used. In general, these procedures were the same as or equivalent to recommended methods of the U.S. Environmental Protection Agency (EPA), the American Public Health Association (APHA), or the American Society for Testing and Materials (ASTM). Total residual chlorine was measured using a direct amperometric titration procedure after acidification of the sample to pH 4 and the addition of potassium iodide [6]. The lower detection limit was 3 µg chlorine/litre.

The study approach followed was first, to define the area in which the WWTP effluent was mixing with the river ("zone of mixing") using specific conductance corrected for background levels as a conservative tracer. Then, fathead minnows *(Pimephales promelas)* were placed in cages, described by Lee et al. [5] and Newbry and Lee [7], upstream of the discharge and inside and outside the zone of mixing to help define a zone of passage and to describe the severity of the impact of the discharge on fish forced to stay in one location. Concentrations of chlorine, ammonia, and nitrite, the pH, temperature, and other parameters were measured at intervals of several hours at each of the cages in an attempt to correlate the overall exposure of the fish with the observed mortality rate. Water samples were collected as far as 50 river km downstream

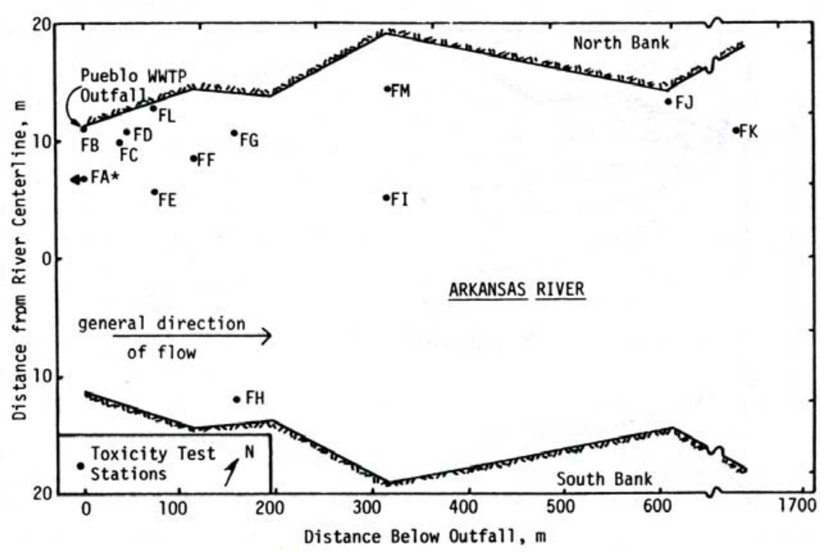

FIG. 2—*Locations of the fish toxicity test stations—schematic view (after Lee et al [5]).*

in order to evaluate the contaminant persistence and transformation.

Results

Lee et al. [5] presented the entire set of data collected during the study; presented in the following sections is a discussion of the key findings of the study.

Mixing

Figure 3 illustrates the mixing pattern of the Pueblo WWTP effluent with the receiving water based on specific conductance profiles. The dashed lines represent generalized isoconcentration lines and show how the effluent hugged the north bank and was gradually laterally dispersed. Complete mixing of the effluent with the river water so that there was essentially no concentration gradient across the river did not occur until about 4.5 km downstream during the study period.

Chlorine

Chlorine is used at the Pueblo WWTP for partial disinfection of the effluent. Because of the high levels of ammonia present, the residual chlorine is in the form of combined chlorine, principally monochloramine. The standard practice at the treatment plant was to partially dechlorinate the effluent, using sulfur dioxide, prior to the discharge of the effluent into the river in order to maintain effluent levels below 0.5 mg chlorine/litre. Through special provisions made for this study, the plant was operated

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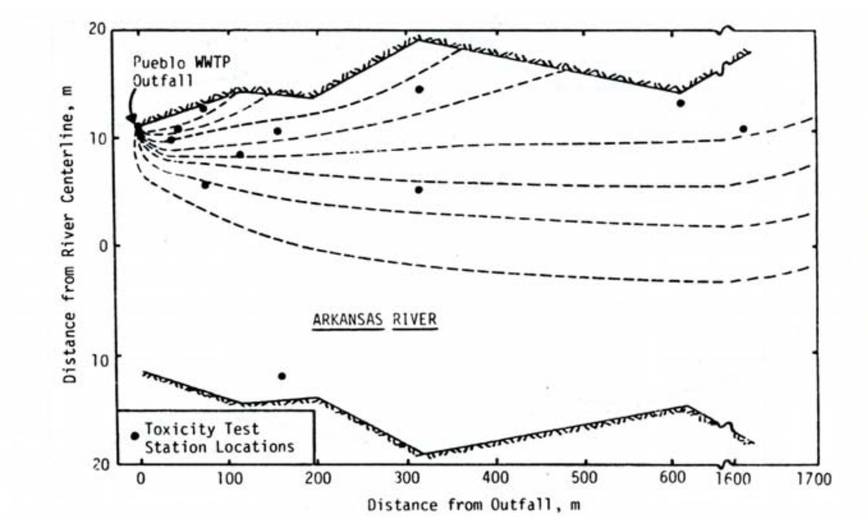

FIG. 3—*Conceptual mixing pattern based on specific conductance profiles* (*after Lee et al* [5]).

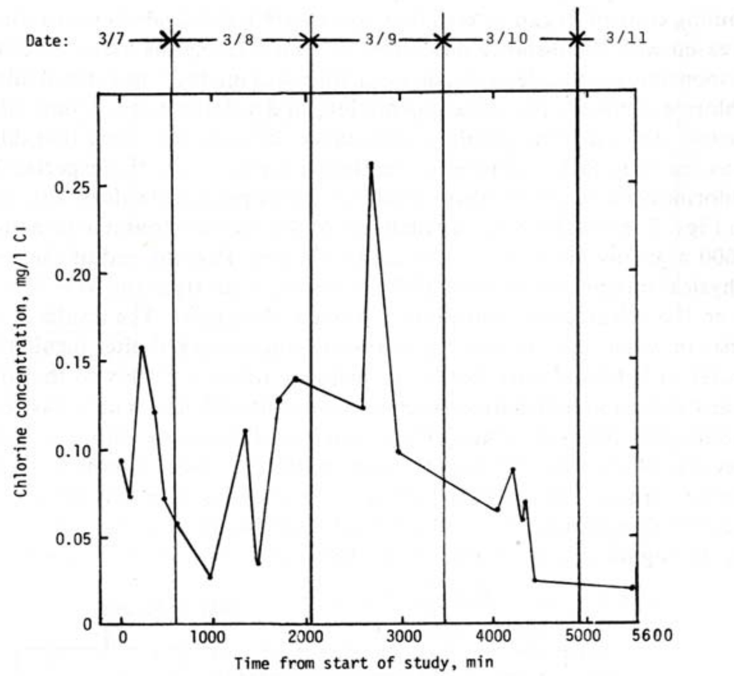

FIG. 4—*Outfall (Station FB) chlorine concentrations over time when the WWTP was practicing partial dechlorination (after Lee et al [5]).*

as usual for the first 5 days of the study; dechlorination was terminated for the study on the last day.

As shown in Fig. 4, chlorine concentrations in the WWTP effluent were highly variable during the study period. They ranged from about 0.02 to over 0.25 mg chlorine/litre during the period when the WWTP was partially dechlorinating the effluent. Because the concentrations were so variable, the average concentrations at each station for this period of study were weighted based on time. The concentrations were plotted as a function of time, the area under the curve was determined, and the resulting number was divided by the amount of time in the entire period. The time-weighted mean concentrations of chlorine and associated 95 percent confidence intervals (generally based on five to ten measurements) during the period when partial dechlorination was being practiced are shown over the distance downstream of the WWTP discharge in Figs. 5 and 6; the mean upstream concentration was 0.011 mg chlorine/litre, with a standard deviation of 0.004 mg/litre based on eleven measurements. This upstream level was probably due to discharges from an electric power generating station which uses chlorine for condenser fouling control. It can be seen that, as expected, the mean concentration decreased with the distance downstream. To determine the major mechanism responsible for this decrease, an evaluation was made of the roles of dilution, chlorine demand, phototransformation, and volatilization. Using dilution factors derived from specific conductance data and assuming that dilution was the only factor causing decreasing concentrations, the expected mean chlorine concentrations were calculated. These predicted values, also plotted in Figs. 5 and 6, show that virtually all of the decrease found within the first 2600 m below the WWTP was due to dilution. Past the end of the zone of physical mixing and dilution (4.3 km downstream from the WWTP), however, the chlorine concentration continued to decrease. The results of bottle tests in which the chlorine concentration was measured after incubation of water in light and dark bottles suspended in the river showed that phototransformation with a first-order rate constant of 0.0004 min^{-1}(base e), was responsible for little, if any, of the observed dissipation. This was expected because of the relatively high turbidity of the river water [about 60 nephelometric turbidity units (NTU)] at the site of the tests. The first-order volatilization rate constant of the chlorine, calculated using an approach developed by Tsivoglou [8], was 0.0019 min^{-1} (base e) at 10ºC, which accounted for over one half of the dissipation

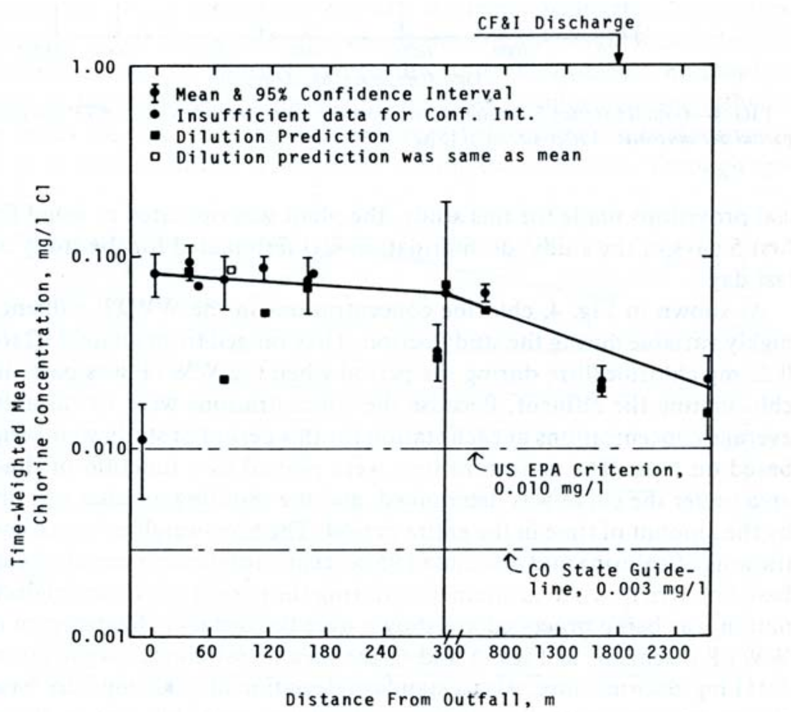

FIG. 5—*Time-weighted mean chlorine concentrations within the zone of mixing* (*after Lee et al* [5]).

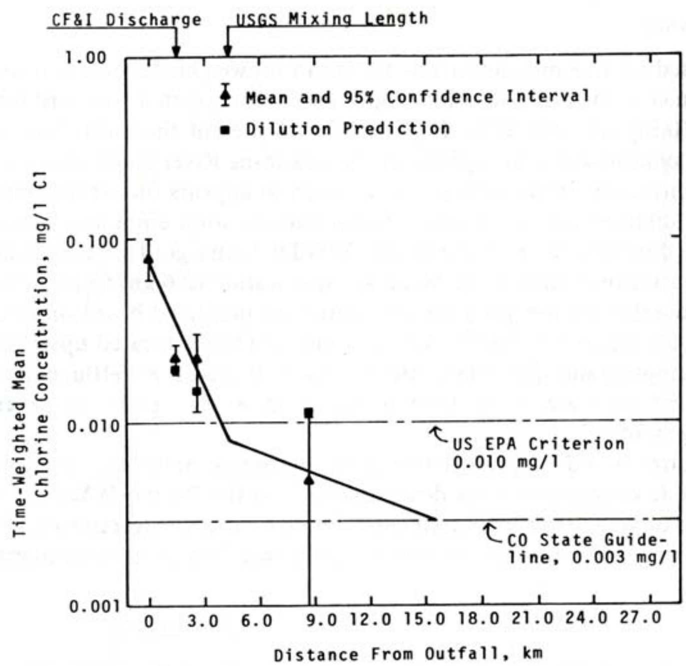

FIG. 6—*Time-weighted mean chlorine concentrations over the study area (after Lee et al* [5]).

due to factors other than dilution. The first-order rate constants determined for chlorine demand (0.0012 min^{-1}) and phototransformation made up the other half. The observed and estimated chlorine dissipation rate constants were in excellent agreement.

The EPA "Red Book" chlorine criterion [9] for the protection of warm-water fish is 0.01 mg chlorine/litre; the current Colorado water quality guideline is 0.003 mg chlorine/litre. Based on conditions existing at the time of the study (essentially worst-case for winter), it was estimated that the Colorado guideline would be exceeded over a distance of 15.4 km downstream of the WWTP discharge; the Red Book value would be met by about 3.9 km downstream, which is within the zone of physical mixing.

Based on work done by the authors during the summer of 1980 on other Colorado Front Range streams, it was predicted that, during worst-case summer conditions in this area of the Arkansas River, the chlorine persistence would be approximately half that found during worst-case winter conditions. It appears that under both worst-case summer and worst-case winter conditions the concentrations of chlorine in the Arkansas River derived from Pueblo WWTP discharges will be in violation of the state standard outside of the zone of physical mixing.

Ammonia

Based on five measurements, the mean (unweighted) upstream total ammonia concentration was 0.30 mg nitrogen/litre, with a standard deviation of 0.10 mg nitrogen/litre. Figures 7 and 8 present the mean (unweighted) total ammonia concentrations in the Arkansas River study area as well as concentration estimates based on dilution. It appears that at the time of the study dilution was the primary factor causing total ammonia levels to decrease downstream from the Pueblo WWTP discharge. That the actual mean concentration found at the Mead Avenue station (2.6 km from outfall) was considerably greater than the concentration predicted based on dilution is probably related to the CF & I steel mill discharge located upstream from this sampling site. The total ammonia levels of the CF & I effluent have been reported by Cain et al [10] to be from a few tenths to several mg nitrogen/litre.

Figures 9 and 10 present the mean un-ionized ammonia concentrations found at various distances downstream from the Pueblo WWTP discharge (based on one to five measurements). Based on four measurements, the mean upstream concentration was 0.009 mg nitrogen/litre, with a standard deviation of 0.003 mg nitrogen/litre. As shown

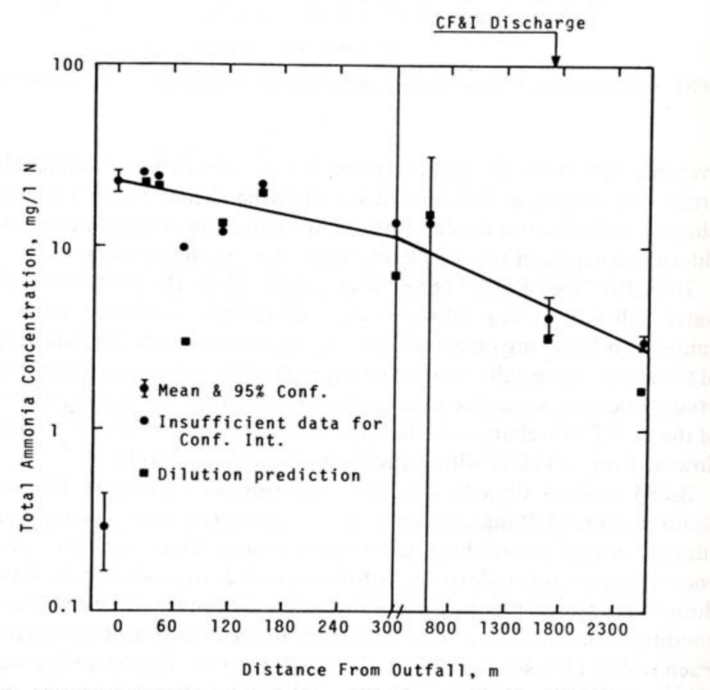

FIG. 7—*Mean total ammonia concentrations within the zone of mixing (after Lee et al [5]).*

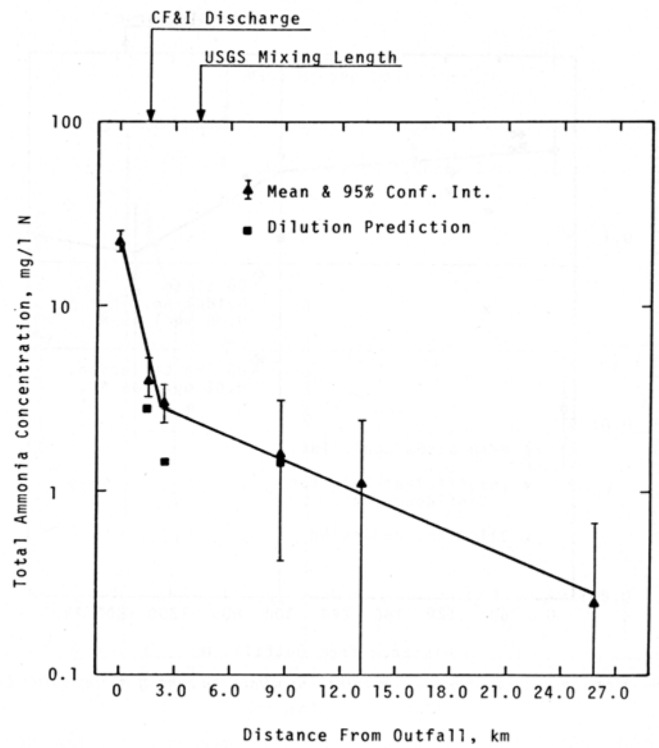

FIG. 8—*Mean total ammonia concentrations over the study area (after Lee et al [5]).*

in these figures, dilution also appears to have been the principal factor responsible for the decrease in un-ionized ammonia concentrations, although the dilution tended to under predict the concentrations found more than it had the total ammonia levels. This is probably the result of pH and temperature values changing with distance downstream of the outfall, which, while not affecting the total ammonia level, would alter its speciation.

As indicated in Figs. 9 and 10, the mean un-ionized ammonia concentrations exceeded both the Colorado guideline for warmwater fish (0.06 mg nitrogen/litre) and the EPA Red Book criterion (0.016 mg nitrogen/litre) on the north side of the river for at least 4000 m downstream of the Pueblo WWTP discharge; the Red Book chronic exposure safe level was exceeded by the mean values for an estimated distance of 15 to 18 km below the discharge. In general, state water quality standards for contaminants such as ammonia are applicable at the edge of the "mixing zone," the extent of which is determined on a case-by-case basis. Since the size of the mixing zone will frequently

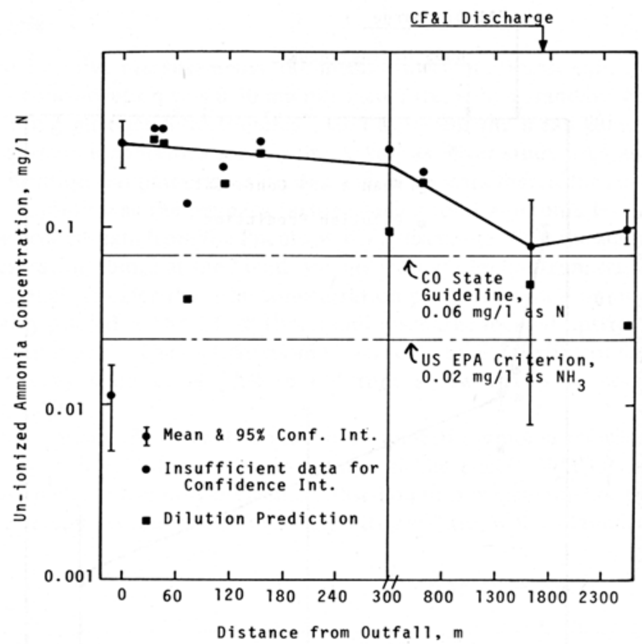

FIG. 9—*Mean un-ionized ammonia concentrations within the zone of mixing (after Lee et al* [5]).

be at least as large as the zone of physical mixing, which in this case (typical of worst-case winter conditions) extended for about 4.3 km, the Pueblo WWTP would not be causing a violation of the state un-ionized ammonia standard applicable to warmwater fisheries. During the summer months it would be expected that there would be some violations of the Colorado standard for un-ionized ammonia outside the zone of physical mixing because of the increased temperatures and pH values in comparison with those prevailing in the winter. Studies of the type reported herein should be conducted during the summer low flow to confirm this, however based on the literature, the values for lethal concentrations killing 50 percent of the test organisms (LC_{50}) in 96 h for un-ionized ammonia range for non salmonids from about 0.35 to 1.24 mg nitrogen/litre [11], while those specifically for fathead minnows have been found to range from about 0.3 to 3.4 mg NH_3/litre (0.7 to 2.8 mg nitrogen/litre). These values were not approached, much less exceeded, in the study area. Therefore, while it does not appear that there will be a problem of acute lethal toxicity due to ammonia, this contaminant could have chronic impacts on aquatic life in the Arkansas River below Pueblo, both within and downstream of the zone of mixing.

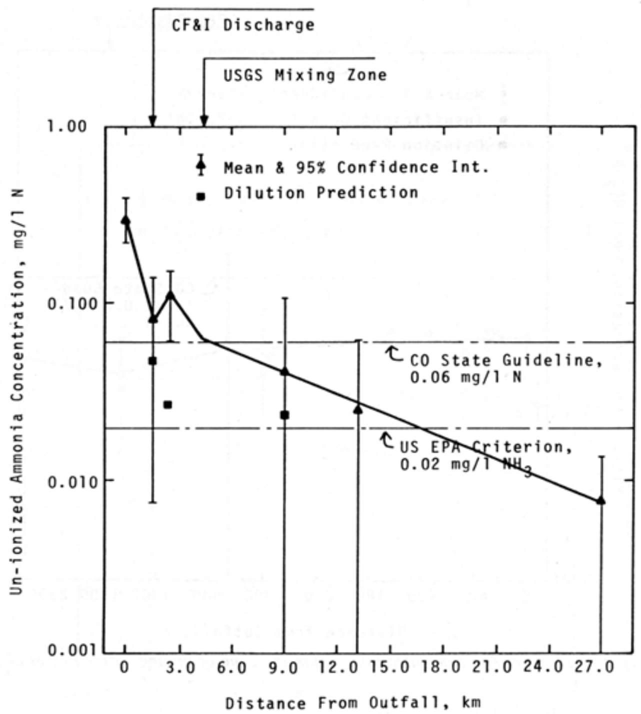

FIG. 10—*Mean un-ionized ammonia concentrations over the study area* (*after Lee et al* [5]).

Nitrite

Nitrite is the intermediate compound in the conversion of ammonia to nitrate, and it can be toxic to aquatic organisms. While nitrite has generally been considered a transient compound in aquatic systems, rarely persisting, and being rapidly converted to nitrate, the data gathered during this study indicate otherwise. Because of the low ambient temperatures of the Arkansas River and the greater sensitivity to lower temperatures of the conversion of nitrite to nitrate than of ammonia to nitrite, a buildup of nitrite occurred downstream of the WWTP discharge. Figures 11 and 12 summarize the averaged nitrite levels measured during the study (generally based on one to five measurements) and the concentrations predicted by the dilution model. Within the first 1630 m downstream of the WWTP, it appears that the NO_2^- concentration decrease was due largely to the dilution of the NO_2^- in its effluent. However. consistently elevated concentrations were found at the stations at 8.5 and 13 km downstream, which was probably due to the conversion of ammonia to nitrite. That this conversion was not noted when the ammonia

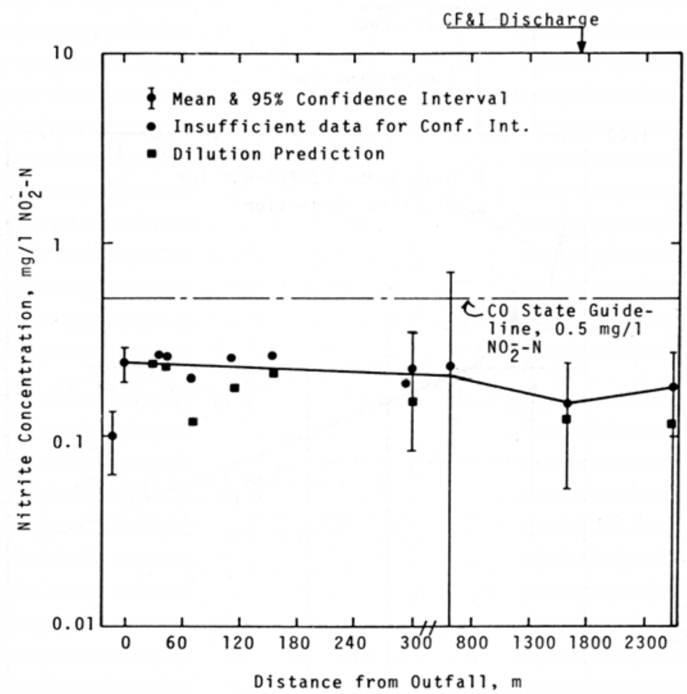

FIG. 11—*Mean nitrite concentrations within the zone of mixing (after Lee et al* [5]).

data were reviewed is not unexpected since those values were in the range of milligrams of nitrogen per litre to tens of milligrams of nitrogen per litre, while nitrite levels were at the tenth of a milligram of nitrogen per litre level.

At this time Colorado is the only state which has numerical water quality guidelines for nitrite. For warmwater aquatic life this guideline is 0.5 mg nitrogen/litre; however, as discussed by Lee et al. [5], there is little technical justification for this value; it may be too strict or too lenient. The significance of nitrite in affecting beneficial uses of the Arkansas River near Pueblo is unknown at this time since concentrations of nitrite derived primarily from the WWTP effluent ammonia were found to be on the order of several tenths of a milligram of nitrogen per litre at considerable distances from the Pueblo WWTP discharge and since with further study it may be found that the chronic safe limit of nitrite for warm water is less than values that have been found in the river during these studies.

Fish Toxicity

The results of the *in situ* fish toxicity tests are summarized in Table 1. No mortality was observed at the upstream control station (FA), the cross-stream (zone of passage)

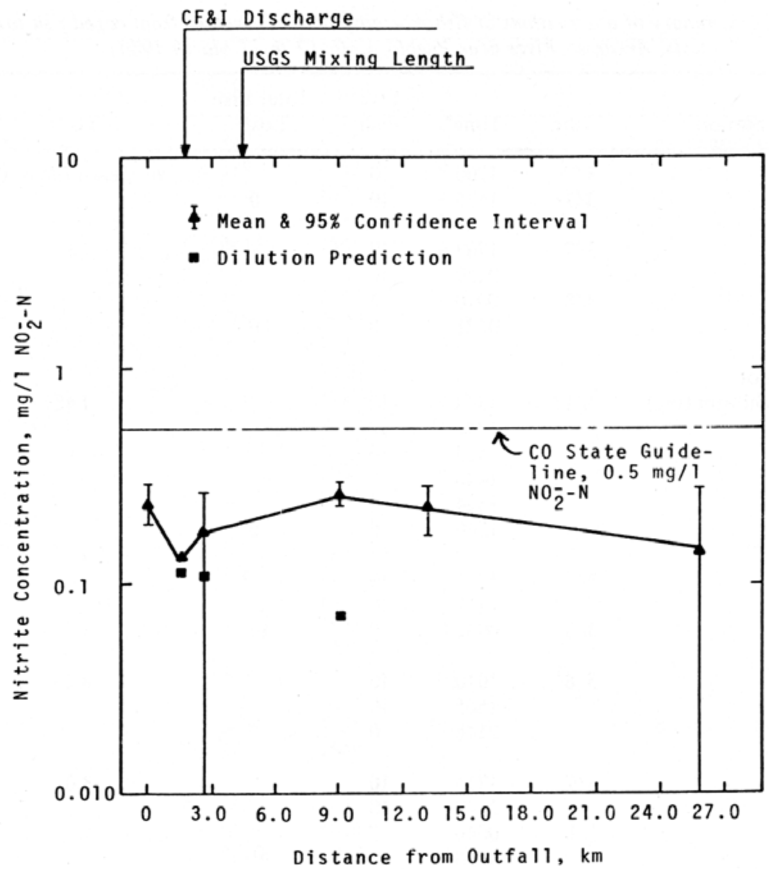

FIG. 12—*Mean nitrite concentrations over the study area* (*after Lee et al* [5]).

control station (FH), or the station farthest down-stream (FK). Rapid death occurred, however, of all the test fish placed at the outfall station (FB). When partial dechlorination was being practiced at the WWTP, the time-weighted average effluent chlorine concentration at the outfall was 0.08 mg chlorine/litre, all the fish placed there were dead within 13 h of exposure. The tests run after dechlorination was terminated showed an average chlorine concentration of 0.6 mg/litre, with all the caged fish having died within about 2 h of exposure. As noted previously in the description of the mixing of the effluent and river water, there were marked concentration gradients across the river downstream of the WWTP discharge, as was reflected by the caged fish mortality patterns. Higher chlorine concentrations and greater mortality were found at Station FJ, 615 m from the outfall, than at FI, 316 m from the outfall; no mortality was found in 94 h of exposure at Station FH, which was the same distance downstream as Station FG, where 100 percent mortality was found within 41 h.

TABLE 1—*Summary of observations of fish mortality and LT_{50} values from caged fish toxicity tests, Arkansas River near Pueblo, Colo. (7 to 11 March 1980).*

Station	Date	Time[a]	Live Fish	Total Fish Lost[b]	LT_{50}, h
FA	3/7	1700	10		no death (94.6 h)
	3/11	1535	10	0	
FB	3/7	1703	10		7.1
		2157	10		
	3/8	0010	5		
		0621	0	0	
FB (not dechlorinating)	3/11	1334	10		1.48
		1349	10		
		1423	10		
		1448	8		
		1524	2		
		1540	0	0	
FC	3/7	1712	10		...
		2150	10		
	3/8	0032	0	10	
FD	3/8	1010	10		8.2
		1505	10		
		2148	0	0	
FE	3/7	1716	10		38.0
		2143	10		
	3/8	0040	9	1	
		0626	9		
		1511	9		
		2154	9		
	3/9	1007	4		
		1604	3		
	3/10	0928	1		
		1550	0		
FF	3/7	1735	10		30.0
		2135	10		
	3/8	0045	10		
		0633	10		
		1516	10		
		2157	6		
	3/9	1011	0	0	
FG	3/7	1738	10		25.0
		2121	10		
	3/8	0055	10		
		0644	8		
		1521	8		
		2205	1		
	3/9	1020	0		

TABLE 1—*Continued.*

Station	Date	Time[a]	Live Fish	Total Fish Lost[b]	LT_{50}, h
FH	3/7	1738	10		no death (94.3 h)
	3/9	2118	9	1	
		1027	9		
		1616	5	4	
	3/11	1545	5		
FI	3/7	1747	10		91.0
	3/8	1120	10		
		1532	10		
		2220	9	1	
	3/9	1027	9		
		1630	9		
	3/10	1005	7		
		1605	6		
	3/11	1003	5		
FJ	3/7	1755	10		19.0
	3/8	1110	6		
		1606	5		
		1855	3		
		2238	2		
	3/9	1105	0	0	
FK	3/7	1835	10		no death (94.1 h)
	3/11	1640	10		
FL	3/9	1240	10		12.2
		1611	10		
	3/10	0933	0	0	
FM	3/9	1247	10		20.0
		1628	10		
	3/10	0957	1		
		1610	0	0	

[a] Generally, the only times reported here were those when the death of fish was noted or at the first and last observation. Observations of fish were generally made every several hours at stations closest to the outfall.

[b] Fish loss attributed to escape during observation or removal of accumulated sediment. Data from Lee et al [*5*].

Unlike most standard laboratory acute lethal toxicity tests, the *in situ* toxicity tests conducted assess the actual, short-term, worst-case impacts on fish at a particular location and under the conditions of variable concentrations of contaminants and of the contaminant mixtures present in the river. With so many variables, however, it is more difficult to reduce the data obtained from *in situ* tests to a common basis that can be used for comparison of toxicity and other factors, analogous to the LC_{50} values, for example,.obtained from laboratory tests. In an attempt to reduce the mortality data to a more readily usable form, "LT_{50}"values were computed for each toxicity test station.

The LT_{50} is the time required for 50 percent of the caged test organisms to die at each of the stations. To relate that time to the contaminant concentration which was responsible for the toxicity, the time-weighted average concentrations of chlorine, the contaminant most likely to have been responsible for the greatest part of the impact, for each station was computed. These data are included in Table 1 and are summarized in Fig. 13. The fish lost through escape were not included in the computations. The method of data plotting in this figure is fashioned after the "concentration of available forms-duration of organism exposure-no impact" relationships described by Lee et al [3,4]. It can be seen that the data follow the general pattern they describe, that is, that organisms can tolerate higher concentrations when the duration of exposure is shorter.

From inspection of Fig. 13 it appears that if chlorine were the only contaminant causing acute lethal toxicity in the river, the 96-h LC_{50} for the time-weighted average chlorine concentration would be about 0.03 mg chlorine/litre. This estimate is based on a single point on the concentration-duration of exposure curve; it is possible that the "true" 96-h LC_{50} for the average concentration and concentration pattern observed is between 0.03 and 0.07 mg chlorine/litre. These values are similar to the LC_{50} values reported in the literature based on laboratory studies of the toxicity of chlorinated

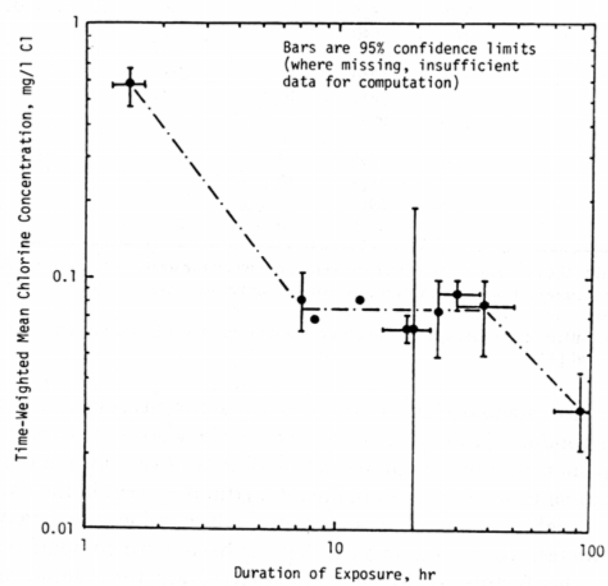

FIG. 13—*Time-weighted mean river chlorine concentration–duration of exposure–50 percent mortality relationship for fathead minnows in the Arkansas River below Pueblo* (*after Lee et al* [5]).

domestic wastewater effluents to fathead minnows (0.108 mg chlorine/litre, Arthur et al. [12]; 0.089 mg chlorine/litre, Ward et al. [13]. Brungs [14], in his review of the literature, indicated that the reported range of 96-h LC_{50} values for fat-head minnows exposed to chlorine was 0.05 to 0.16 mg chlorine/litre. The average chlorine concentrations at which 50 percent mortality was observed within 96 h during the current study were slightly lower than these reported values, which suggests that additional factors may have been exerting toxic effects or that the high concentrations experienced had a greater adverse impact than the low concentrations had an assuaging impact. If a greater number of chlorine residual measurements had been made, it may have been possible to weight the elevated concentrations in proportion to the laboratory-derived concentration-duration of exposure relationship for chlorine. However, even with the variability and complexity of the system and the shortcomings of averaging the data, the similarity of the 96-h LC_{50} values derived for chlorine (and chloramine) in the laboratory and the averaged concentration computed to kill 50 percent of the test organisms in the river in 96 h was remarkable.

Implications of the Hazard Assessment for Water Quality Management in the Arkansas River Near Pueblo

In order to begin a hazard assessment for a chemical, the desired beneficial uses of the receiving water must be defined. The three primary beneficial uses of potential concern for the study reach of the Arkansas River are domestic water supply, irrigation, and a warmwater fishery. The primary area of concern in the Arkansas River for this study is the warmwater fishery potential beneficial use. This beneficial use actually has a broader-scale implication since water bodies that will support warmwater fisheries will typically support a wide range of beneficial uses, including domestic water supply (except that a few contaminants, notably nitrate, will adversely affect other beneficial uses before a warmwater fishery is impaired).

Based on the results of this study, it appears that within a 7000 m` area, extending about 1000 m downstream from the outfall and one third of the river width from the north bank, there would be a possibility of desirable fish experiencing acute, toxic effects if they remain in the area on the order of several days. The potential for adverse effects to fish entering that area may be lessened by their acclimation to the contaminants present through a prior sublethal exposure or by a short duration of exposure in the area but is increased during cold weather by the possibility that fish would be attracted to the area because of the warm effluent. Several investigators have found that acclimation occurs with both ammonia and chlorine. Lloyd and Orr [15] found that rainbow trout previously exposed to sublethal concentrations of un-ionized ammonia could then be exposed, with no apparent adverse effects, to concentrations that were lethal to fish not previously exposed to ammonia. A similar finding was reported by Redner and Stickney [16] with *Tilapia aurea.* Thurston and Russo [17], in their review of the literature, summarized additional studies in which acclimation to ammonia was found to occur. DeGraeve and Ward [18] found that after exposure to sublethal concentrations of chlorine, fathead minnows were able to survive concentrations in excess of the 96-h LC_{50} for unacclimated fish.

While the literature on the avoidance response is not definitive, it appears that fish species may avoid high to moderate levels of chlorine and possibly low levels as well [19,20]. In recently completed work by the authors on the impact of the chlorine and ammonia in the wastewater discharge of Fort Collins, Colo., on the beneficial uses of the Poudre River, it was found that resident fish captured near (within 100 m or so) the wastewater treatment plant discharge were effectively avoiding exposure to deleterious contaminant concentrations, since they died within a few days of being placed in cages in the effluent plume in the river, whereas upstream controls survived. Observations of the resident fish in the region of the effluent discharge showed that these fish were making excursions into the regions with elevated chlorine concentrations. It may, therefore, be concluded that they are not being completely repelled by the chlorine but apparently have a mechanism by which to avoid acutely lethal exposure. These observations are important for "zone of passage" considerations in that, at least under certain circumstances, the fish can pass without significant impact through a region containing concentrations of contaminants which would be acutely lethal to them under conditions of continuous exposure for several days. Resident fish studies of the type that are currently being conducted in Fort Collins should also be conducted in Pueblo.

The results of the Pueblo study also indicated that there exists, during near-worst-case winter conditions, a zone of passage through the mixing region downstream from the Pueblo WWTP outfall in which fathead minnows can survive with no apparent adverse effects for at least 4 days of exposure. At each transect established for this study, the contaminant concentrations over at least one third of the lateral transect distance were less than the concentration required to kill fathead minnows within 4 days of constant exposure. This zone of passage probably exists for resident warmwater game fish as well.

It is uncertain what long-term effects to fathead minnows or other fish would result from continuous exposure to contaminants within the zone of mixing but outside the region of potential short-term lethal effects. Throughout most or all of this river reach, both the EPA Red Book criteria and the Colorado State water quality guidelines for chlorine and un-ionized ammonia in water bodies (that is, chronic safe levels) designated for warmwater fisheries support are exceeded, which indicates that the potential for chronic impacts exists. It is probable that some adverse effects could be found but that these would be likely to be restricted to a particular life stage of fish (for example, the fry stage) or would be manifested after an extended period of exposure. Additional studies would be needed to determine the effects of short-term and long-term exposure of different life stages of fathead minnows and other species of fish, as well as other aquatic organisms, to these lower contaminant concentrations in order to detect adverse impacts and to assess the significance of these impacts on beneficial uses of the Arkansas River.

Before studies such as those suggested are conducted, a determination should be made of the type of warmwater fishery that is desired. In keeping with the goals of Public Law 92-500 (the 1972 amendments to the Federal Water Pollution Control Act), it should be a system in which several types of warmwater fish are represented, although not necessarily in sufficient numbers to constitute a potential recreational resource and not necessarily within the zone of mixing. The support of any fishery would be largely dependent on the availability of a suitable physical habitat, which could be estimated by methods such as those developed by the Instream Flow Group of the U.S. Department of the Interior, located in Fort Collins, Colo. [21]. Habitat analyses and fish population surveys should be made during several periods of the year, including late winter and late summer (minimum flow conditions). Information from these studies could be used to estimate the size of the existing population and its composition, as well as the potential for development of a larger population associated with implementation of alternative water quality management practices.

A limited amount of information of this type is currently available for the Arkansas River near Pueblo, Colo. With a minimum flow maintained throughout the year, it is likely that an adequate habitat exists to support a population of warmwater game fish throughout most of the reach of the Arkansas River evaluated in this study. It is reasonable to expect that a limited warmwater sport fishery could exist in the Arkansas River below the Pueblo WWTP discharge. In the opinion of the authors, it is certainly inappropriate for the Colorado Water Quality Control Commission to assign a nonaquatic life classification to the Arkansas River below Pueblo. As noted previously, this does not mean that the authors feel that there is a potential for developing a significant warmwater sports fishery in the Arkansas River below Pueblo. Although the reach of the Arkansas River evaluated in the present study is located near the city of Pueblo, and thus has the potential for recreational use by a large number of people, at the present time there is limited public access to the river in this area. For this reason, little if any recreational use is being made of the Arkansas River in the region potentially impacted by the Pueblo WWTP discharge. Without the expenditure of large amounts of money for habitat improvement and for acquisition of public access to the river below Pueblo, the warmwater sports fishery potential of this river under the existing flow regime is severely limited, and the appropriateness of spending large amounts of money for control of chlorine and ammonia in the Pueblo wastewaters is highly questionable.

If a self-sustaining recreational warmwater fishery, as opposed to one that is supported by stocking, is desired, an assessment of the effects of the Pueblo WWTP contaminants on reproduction and fry survival, coupled with an identification of potentially suitable spawning and rearing areas and an investigation of avoidance–attraction of fish to areas of high concentrations of contaminants, should be made. These further tests represent more sophisticated levels of hazard assessment.

A proper hazard assessment for warmwater fishery beneficial use must include an analysis of all potentially important contaminant sources in the area. It is possible that considerable amounts of money could be spent to remove potentially hazardous chemicals from the Pueblo domestic wastewater effluent without a substantial improvement in the beneficial uses of the water because of discharges from another source. As discussed earlier, measurable amounts of chlorine were found in the Arkansas River above the Pueblo WWTP discharge; the source or sources of this chlorine and of other contaminants should be identified and their loads quantified. A potentially significant source of contaminants in the Arkansas River below the city of Pueblo is the CF & I Steel Co. discharge. While at this time no information has been provided to the authors on the characteristics of the CF & I wastewater discharge, steel mill discharges in general contain a wide variety of toxicants which can exert both acute lethal and chronic sublethal toxicity effects on fish. Of particular concern are ammonia, cyanides, and a variety of poorly characterized organic compounds. Based on data presented by Cain et al [10], the ammonia discharged from the CF & I Steel Co. appears to add to the overall ammonia burden of the Arkansas River. The relative significance of ammonia from the Pueblo WWTP and the CF & I Steel Co. discharges could readily be determined, based on data for the concentration, and total loads from each source.

Conclusions

The authors have concluded that even though the Arkansas River below Pueblo has a considerably greater flow than many other Colorado Front Range streams and, therefore, a much greater potential for development of fish and other aquatic life in the river, the severe habitat limitations created by the heavy sand and silt load from Fountain Creek, coupled with limited substrate and poor cover, create a situation in the river which is naturally detrimental to any fish and other aquatic life development of the river below the Pueblo wastewater treatment plant discharge. The authors have further concluded that Pueblo's domestic wastewater discharges will, at times, cause violations of several of the proposed standards outside of the zone of mixing of the effluent with the river. These violations would not constitute legal violations of the standard if the mixing zone of the effluent with the river were sufficiently large. However, if the zone of mixing and the mixing zone are approximately the same size, then the city of Pueblo will have to initiate advanced wastewater treatment at its domestic wastewater treatment plant in order to avoid violating the proposed standards for ammonia, nitrite, and chlorine. The expenditure of funds for advanced wastewater treatment to remove the "excessive" concentrations of these chemicals in the Pueblo domestic wastewater treatment plant effluent will, however, not result in any perceivable benefit to the proposed uses of the river. Therefore, the cost-effectiveness of these proposed actions must be questioned.

Acknowledgments

This investigation was supported by the U.S. Environmental Protection Agency Region VIII's Section 201 funding, requested and administered by the Pueblo Area Council of Governments (PACOG). Support was also provided by EnviroQual Consultants & Laboratories, Fort Collins, Colo. D. Cain, of the Pueblo Subdistrict of the U.S. Geological Survey, provided background information on the Arkansas River and data collected by the USGS during their mixing zone study on the Arkansas River, which was conducted concurrently with this study. The assistance of Dr. S. Tobita, of Yamanashi Institute for Public Health, Kofu, Japan, in conducting the field studies is also appreciated.

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