CHAPTER 102

STUDIES ON THE WATER QUALITY HAZARD OF CHLORINE IN DOMESTIC WASTEWATER TREATMENT PLANT EFFLUENTS

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INTRODUCTION

Chlorine is widely used for partial disinfection of municipal wastewater treatment plant (WWTP) effluents. To achieve satisfactory disinfection, as indicated by suitable reduction in fecal coliform concentrations, an effluent residual chlorine concentration of several tenths of a milligram of chlorine per liter or more is often required. These chlorine concentrations are several orders of magnitude higher than those known to be toxic to certain fish species.[1,2] Therefore, where chlorinated effluent is discharged, the potential exists for adverse effects on fish residing in the receiving water body.

One method for mitigating the potential adverse impacts of chlorine on receiving water bodies is to dechlorinate the WWTP effluent. Dechlorination essentially eliminates the toxicity of chlorinated effluents.[3,4] Dechlorination, however, also increases the cost of wastewater treatment on the order of \$0.003/m^3 (\$0.01 per 1000 gal) of wastewater treated. Thus, the amount of potential beneficial use enhancement that can be achieved through this

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additional expenditure for wastewater treatment should be determined.

A series of studies was conducted to directly determine the effects of chlorinated WWTP effluent on fish in selected Colorado Front Range river systems. This chapter summarizes the results of these studies. The complete data and additional discussion of the studies, their results, and the implications of the results for water quality management are provided by Lee et al.[8-9] and Newhry.[10]

STUDY DESCRIPTION AND METHODOLOGY

Study Locations

Studies were performed in four Colorado Front Range rivers: Cache la Poudre River, into which Fort Collins WWTPs 1 and 2 discharge; Big Thompson River, into which the Loveland WWTP discharges; Arkansas River, into which the Pueblo WWTP discharges; and Fountain Creek, into which the Colorado Springs WWTP discharges. In each case, the primary study area was the river reach near the particular WWTP outfall, extending from several meters above the outfall to several hundred meters or more below the outfall.

General Approach

The hazard assessment approach described by Lee et al.[11,12] and Newbry[10] was followed for each study in the series. Basically, this approach entails conducting specific information gathering and analysis activities sequentially until the extent of impairment of the designated beneficial uses of the receiving water, resulting from the discharge treated in a given manner, can be defined with enough certainty to make management decisions. Information-gathering activities included effluent and in-stream contaminant concentration measurements, WWTP effluent-river mixing analysis, in-stream toxicity tests, and fish census and habitat characterization. In these studies, the fish census and habitat information was provided by other investigators. Emphasis was placed on collecting data during summer and winter low-flow (worst-case) conditions; where possible, data were collected for a range of flow and environmental conditions. These data were used to evaluate seasonal and other effects on chlorine toxicity and the fate and persistence of this contaminant.

Effluent-River Mixing Analyses

Measurements to determine the rate of lateral (cross-stream) and longitudinal (downstream) mixing of the WWTP effluent with the river were made during each study. Tracers used included temperature, specific conductance, and Rhodamine B dye. The appropriate tracers were measured across selected river transects within each river reach upstream and with distance downstream of the WWTP discharge. Comparisons among the mixing estimates obtained by using these three tracers showed that all yielded essentially equivalent results. The mixing data were used with chlorine concentration data to estimate and plot chlorine isoconcentration contours downstream from the WWTP outfalls, and to evaluate the reactivity of the chlorine. The approach used is detailed in Lee et al.[5-9] and Newbry.[10]

Chlorine Measurements

Chlorine concentrations were measured by using a modification of Standard Methods,[13] Method 409C, Amperometric Titration Procedure, for total chlorine. Details of the procedure used are presented by Lee et al.[14] Except for the strength of the phenylarsine oxide and the titration endpoint determination procedure, this method is identical to the U.S. Environmental Protection Agency (EPA)[15] Method 330.1, chlorine procedure. Chlorine concentrations as low as 0.005 mg/L Cl were accurately measured when using this method.

In-Stream Toxicity Tests

Toxicity tests were performed in the receiving waters by using fish cages constructed as shown in Figure 1. Design and use of these cages have been described by Newbry and

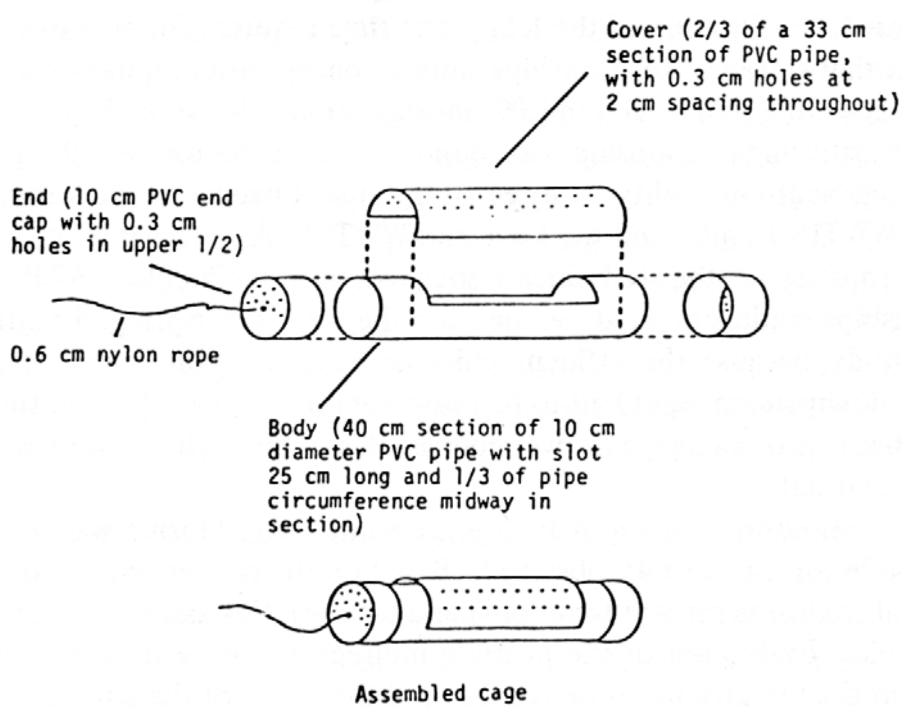

Figure 1. In-stream fish toxicity cage.

Lee.[16] The cages were placed at locations in the river reach, which were selected on the basis of contaminant concentrations and mixing characteristics of the particular reach. An upstream control cage, a series of cages with distance downstream of the discharge, and cages at downstream locations outside the effluent-river mixing areas were generally included at all sites.

The test fish used were fathead minnows *(Pimephales promelas).* A stock supply of test fish was maintained in the laboratory, where the required number of fish needed for a study was acclimated to the anticipated river temperature before use. Toxicity testing was initiated by placing 10 fish in each fish cage. Periodic observations were made to determine mortality and to remove dead fish. Tests generally lasted for 4 d or more. The data collected were analyzed to determine LT_{50} values (i.e., the duration of exposure required to kill 50% of the caged fish) by using the Litchfield-Wilcoxon procedure.[17]

RESULTS AND DISCUSSION

For each study, about six fish cage situations were established. For the first couple of days after the toxicity tests were initiated, observations of fish mortality and chlorine measurements were made every few hours; thereafter, observations and measurements were made at least twice each day. The chlorine concentrations at each cage site were plotted as a function of time; the area under the curve was divided by the total time to provide the aver age chlorine concentration. The average concentration at each station was plotted as a function of the LT_{50}, the time required for 50% of the fish to die at that station. Relationships among concentration, duration of exposure, and 50% mortality (and 0% mortalit^y^) are shown in Figure 2. A single straight-line relationship was found to be suitable for describing given percentage acute mortality at three study areas (associated with the Fort Collins WWTPs 1 and 2 and the Loveland WWTP). A different relationship was appropriate for the study area associated with the Pueblo WWTP. Such relationships could not be developed for the Colorado Springs-Fountain Creek study, because the effluent chlorine concentrations varied greatly and the downstream cages had to be moved about halfway through the study period because of a change in river course. A 50% mortality was observed at only two stations.

The relationships shown in Figure 2 assume that chlorine was solely responsible for the toxicity observed. Based on the concentrations of other potential toxicants present (ammonia and nitrate), this assumption appeared acceptable. Evaluation of the possible indirect influence of ammonia and nitrate in the toxicity response was beyond the scope of the studies.

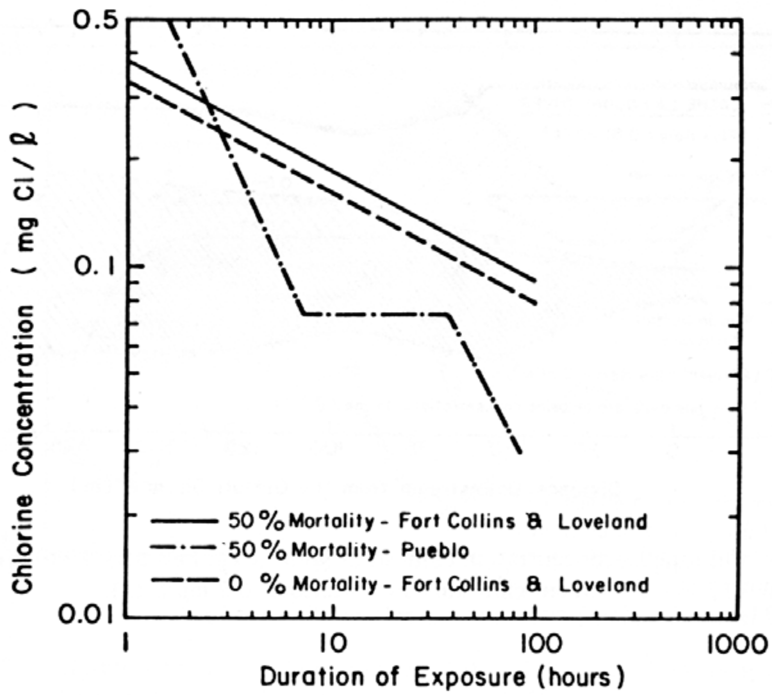

Figure 2. Chlorine concentration–duration of exposure–50% mortality relationships.

Analysis of the chlorine concentration data collected showed that chlorine was essentially conservative (i.e., nonreactive) within the zones of physical mixing of WWTP effluents with the respective river waters. It was concluded that chlorine isoconcentration profiles could be established for these zones directly from mixing data and WWTP effluent chlorine concentrations.

The 96-h LC_{50} is a commonly used expression for describing acute lethal toxicity in the water quality management field. Mortality and concentration data found at the Fort Collins and Loveland study sites indicated that the 96-h LC_{50} value for chlorine (the concentration that will cause 50% mortality in 96 h, which is the same as the concentration necessary to achieve an LT_{50} of 96 h) was 0.093 mg/L Cl; the lower 95% confidence limit for this value was 0.042 mg/L Cl. At the Pueblo WWTP study area, the 96-h LC_{50} value was 0.03 mg/L Cl. These 96-h LC_{50} values for chlorine are similar to those reported in the literature for laboratory tests with fathead minnows, which lend further support to the assumption made that chlorine was the sole toxicant in these systems.

Figures 3 through 5 show the chlorine isoconcentration contours at the Fort Collins and Loveland sites corresponding to 0.093 and 0.042 mg/L. They were developed by using an average effluent chlorine concentration for the particular WWTP and the mixing information for worst-case flow conditions. Figure 6 illustrates an analogous contour for the Pueblo study site. The shaded area in each of these figures shows the zones wherein the

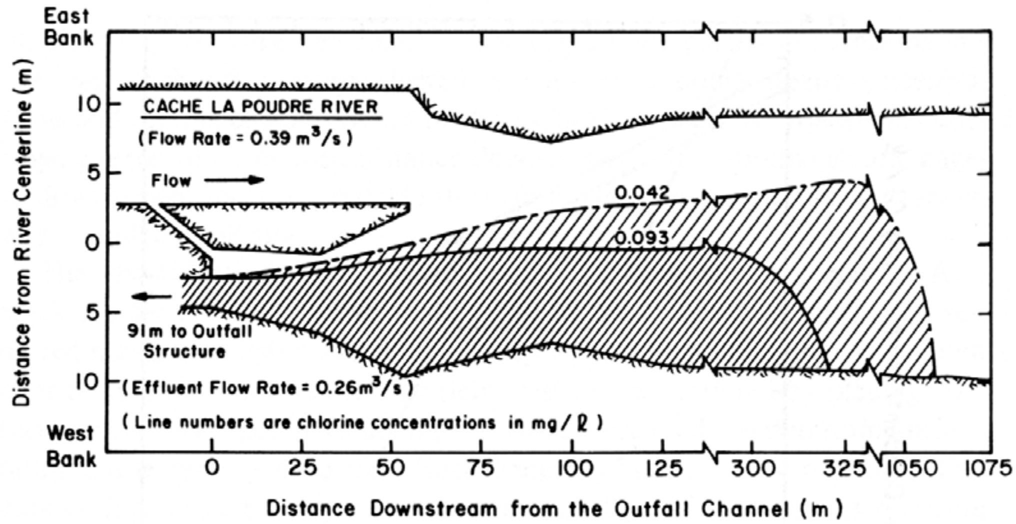

Figure 3. Chlorine isoconcentration contour at 96-h LC_{50}, February 1980, Fort Collins WWTP No. 1 (effluent chlorine concentration: 0.2 mg/L Cl).

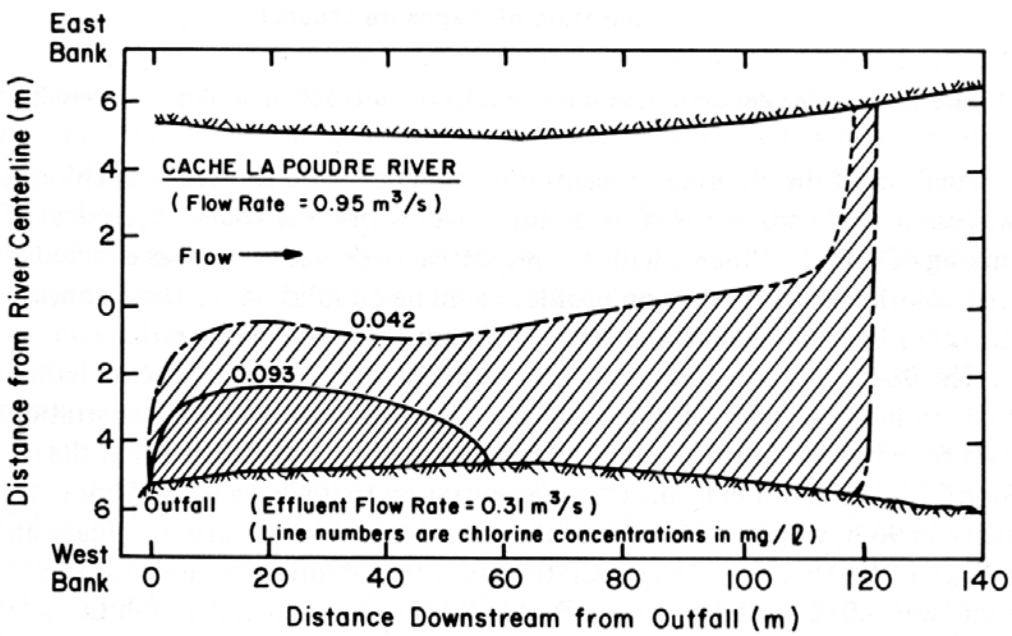

Figure 4. Chlorine isoconcentration contour at 96-h LC_{50}, October 1979, Fort Collins WWTP No. 2 (effluent chlorine concentration: 0.2 mg/L Cl).

mean 96-h LC_{50} values and lower 95% confidence values are exceeded. These zones can be used as first-cut estimates of zones wherein acute lethal (50% mortality) toxicity may occur to fish residing there continuously for several days because the estimated average chlorine 96-h LC_0 was 0.081 mg/L Cl.

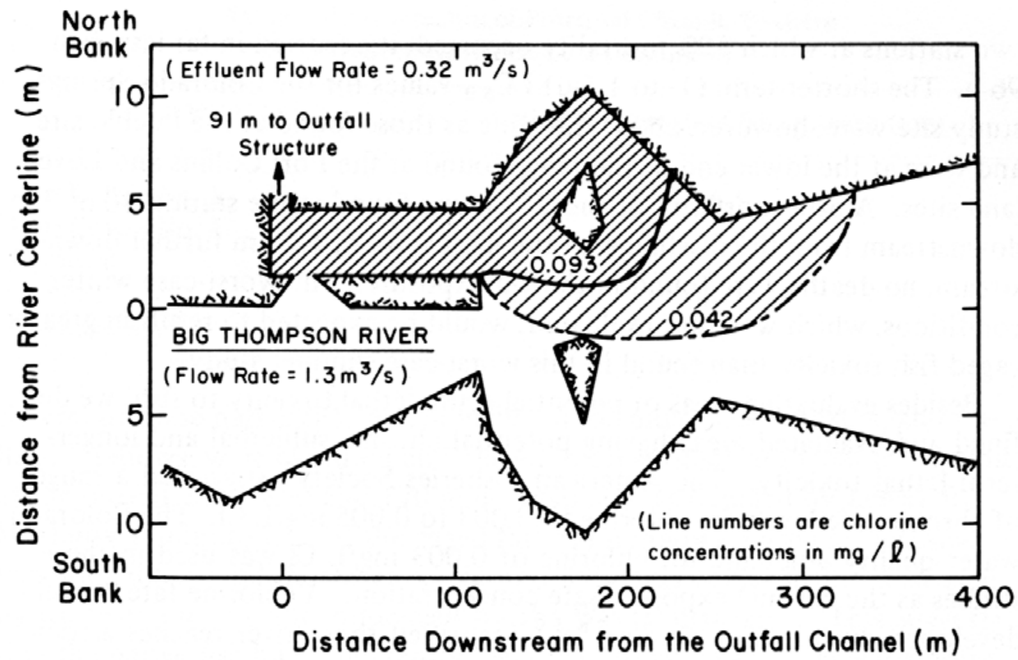

Figure 5. Chlorine isoconcentration contour at 96-h LC_{50}, April 1980, Loveland WWTP (effluent chlorine concentration: 0.2 mg/L Cl).

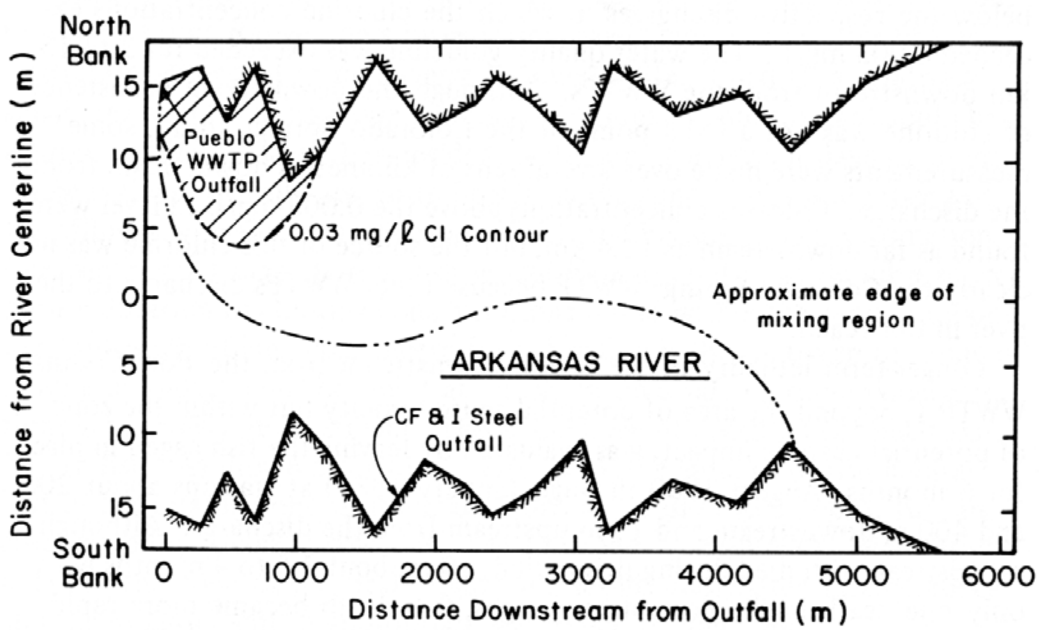

Figure 6. Chlorine isoconcentration contour at 96-h LC_{50}, March 1980, Pueblo WWTP (effluent chlorine concentration: 0.08 mg/L Cl).

Also illustrated in Figures 3 through 6 are the "zones of passage" past the effluent discharges. Fish caged in these areas showed no acute mortality. Derivations of Figures 2 through 6 are detailed by Lee et al.[7] and Newbry.[10]

No 96-h LC_{50} values or concentrations corresponding to an LT_{50} of 96 h could be calculated for the Colorado Springs site because, at the only two stations at which 50%

mortality occurred, it occurred in far less than 96 h. The shorter-term (1- to 1.5-d) LC_{50} values for the Colorado Springs study site were, however, about the same as those found at the Pueblo site and were at the lower end of the range found at the Fort Collins and Loveland sites. A 50% mortality of caged fish was found at the station 40 m downstream from the discharge; at the next station, 1.2 km further downstream, no deaths were found in the 4-d exposure. The worst-case winter conditions, which were not evaluated, would be expected to result in greater caged fish toxicity than found in this worst-case summer study.

Besides evaluating areas of potential acute lethal toxicity to fish, we defined and evaluated areas having potential chronic sublethal and longer-term lethal toxicity. The American Fisheries Society[2] suggested a range of chronic safe levels for chlorine of 0.003 to 0.005 mg/L Cl. The Colorado water quality guideline for chlorine of 0.003 mg/L Cl was used in these studies as the chronic exposure safe concentration. A chlorine fate model developed during these studies [18,19] identified those river reaches associated with the WWTP discharges for which this concentration was exceeded; we assumed the same effluent concentrations as were assumed when preparing Figures 3 through 6. Table I presents the lengths of the river segments below the respective discharges in which the chlorine concentrations exceeded 0.003 mg/L. The water quality guideline was exceeded for 3 to 15 km downstream from the WWTPs. Although the downstream persistence of chlorine was not a focal point of the Colorado Springs study, some measurements were made over several tens of kilometers downstream from the discharge. Chlorine concentrations above the 0.003 mg/L Cl level were found as far downstream as 12.4 km, but the source of this chlorine was not clearly the Colorado Springs WWTP because other WWTPs discharge to the river in this reach.

Longer-term lethality in the region downstream from the Fort Collins WWTP 1, beyond the area of potential acute toxicity but within the zone of potential chronic impact, was evaluated by leaving the fish caged in place for 6 months (August 1980 through January 1981) at stations about 200 and 400 m downstream and 15 m upstream from the discharge. Although no upstream fish died during this period, after about 3.5 to 4 months with only one death in the downstream cages, fish death became more rapid; in the next 2 months, all but two fish in each cage died. The deaths probably occurred because of lower flow conditions and colder temperatures, causing greater chlorine persistence.

Another aspect of the impact of WWTP chlorine on water quality was evaluated during this study—that is, the ability of fish to avoid acute lethal exposure. We observed native fish foraging in an area below the Fort Collins WWTP where caged fathead minnows had died after 1 to 2 d exposure.

Table I. River Reaches of Potential Chronic Toxicity Under Near-Worst-Case Conditions

WWTP	Estimated Length of River Reach (km)
Fort Collins No. 1	6.1
Fort Collins No. 2	3.0
Loveland	3.2
Pueblo	14.7
Colorado Springs	41.5

Several of these native fish, which included longnose dace, suckers, and fathead minnows, were captured and placed in cages upstream from the out fall, at the outfall, and at 60 and 170 m downstream, as detailed by Lee et al.[7] Mortality similar to that of the caged fathead minnows placed at the same locations was found; however, some mortality was found in the upstream native fish controls not influenced by the WWTP discharge. This suggests that the native fish have apparently "learned" to avoid an adverse exposure duration to chlorine while foraging in areas having acutely lethal levels of chlorine. Similar observations were made by Osborne et al.[20]

The above discussion demonstrates that appreciable reaches of the four Colorado Front Range rivers investigated have chlorine in excess of concentrations expected to be adverse to aquatic life. Further, a relatively small area near each discharge has concentrations of chlorine that could be acutely lethal to fish if they resided in the area for several days or more. These regions typically appear to be within the zone of physical mixing of the effluent with the river. Because of this and because other information (see Newbry[10]) suggests that fish would be expected to avoid adverse exposure duration to chlorine concentrations found within the zone of mixing, the river reach of greatest concern for fish safety is that between the zone of mixing boundary and the point at which chronic safe chlorine concentrations are achieved downstream. This is the zone of potential chronic toxicity to fish. As shown in Figures 3 through 6, the amount of fish habitat lost in the mixing zone is minimal. Further, as discussed above, fish are able to readily forage in this area. Lee and Jones[21] discuss the relationship between the zone of physical mixing and legally designated mixing zones and the development of appropriate water quality standards.

Several important factors need to be considered in evaluating the improvement in beneficial uses that will arise from reducing the size of the zone of potential chronic toxicity. First, the zone of potential chronic toxicity is not a sterile region. It can have appreciable fish populations and provide an important recreational fishery. In this zone, the recreational fishery may be less than what it could be based on the habitat characteristics of the river. Contaminant concentration reductions may also simply result in more favorable conditions for survival and propagation of the organisms present. If the beneficial uses of the river reach could be improved by removing chlorine, based on the zones defined previously, the numbers and types of fish present and habitat characteristics (1) just above the point at which the discharge takes place and (2) below the point at which chlorine concentrations return to below chronic safe levels under worst-case conditions should be determined. If no other potential toxicants are present and if the river habitat characteristics throughout this river reach are essentially constant, one may assume, as a first approximation, that the potential improvement in beneficial uses that would arise from reducing the size of the zone of potential chlorine chronic toxicity would be directly proportional to the areal extent of the region in which the concentration is reduced to chronic safe levels. If the habitat characteristics are not constant throughout this reach, the numbers and types of fish that would be present based on the downstream habitat, if there were no chlorine discharged, would have to be estimated. The physical habitat characterization techniques being developed by the Department of Interior's Instream Flow Group[22] provide a basis on which these evaluations can be made. If other toxicants are present in the zone of potential chronic chlorine toxicity, the beneficial use improvement expected to result in that area from chlorine removal may not be obtained. Evaluations similar to the one outlined herein would have to be undertaken for the other contaminants as well if it is desired to improve the beneficial uses of the area.

The zones of potential chronic toxicity are usually established based on low-flow, worst-case conditions. With higher flows, the zone of potential chronic toxicity would likely be reduced as a result of greater dilution, although higher velocities associated with higher flow may counteract this. Therefore, defining the persistence of chlorine under various flow conditions before decisions are made about improvements in beneficial uses obtainable through contaminant removal would be important. Another factor to consider in making this hazard evaluation is that fisheries downstream from the zone of potential chronic chlorine toxicity may be affected in a positive or negative way by chlorine removal. These secondary ecological effects are not well understood at this time.

A recreational fishery beneficial use also depends on public access. In the case of the Arkansas River, no public access in the zone of potential chlorine chronic toxicity is associated with the Pueblo WWTP discharge because all adjacent lands are privately owned. Therefore, removing chlorine will not impact the publicly accessible recreational fishery in that reach of the river. Public accessibility should be considered when establishing beneficial uses of any reach of a river.

The habitat characteristics of the Colorado Front Range streams studied in this investigation were such that little benefit to the recreational fisheries would he expected to be achieved by removing chlorine from the WWTP effluents. Habitat characteristics of all these rivers are severely impacted by low-flow conditions caused by irrigation diversions, unstable bottom habitat characteristics (i.e., they are meandering streams), shallow water depth. etc. Fish census work[5-8] with electroshocking showed that the numbers and types of fish in river reaches below the WWTP discharges studied, where chlorine and other contaminants would be potentially chronically toxic, were about the same as those found upstream. Therefore, we concluded that little benefit, in terms of a warmwater sports fishery, would accrue from removal of chlorine from any of the five WWTP effluents. These conclusions cannot be translated to any other location. Every area must he evaluated on a site-specific basis.

For those areas where chlorine adversely affects fisheries, the cost-effectiveness of chlorine removal can be evaluated on the basis of cost per unit area of improved stream. Although not directly applicable to the case of chlorine in the Colorado Front Range WWTPs, estimated costs for chlorine removal from the WWTP effluents evaluated under worst-case conditions, expressed as cost per square meter of potential acute lethal and chronic toxicity area eliminated per year, are presented in Table II. Data of this type provide water quality managers with a first-cut basis for establishing management policies and priorities. As discussed above, however, in making such an evaluation, the relative significance of the worst-case conditions for the river reach should be taken into account. Possibly, the worst-case conditions, because of their frequency of occurrence, have only minor ramifications for the beneficial uses of the river reach. This should also be accounted for in the cost-benefit figures. Further discussion of how the technical (toxicity, habitat, fish) data are developed and used in a hazard assessment approach to assess

Table II. Costs for Chlorine Removal per unit area of Potential Toxicity Eliminated[a]

	Estimated Cost ($\$/m^2/yr$) for Elimination of	
WWTP	Potential Acute Toxicity Area	Potential Chronic Toxicity Area
Fort Collins No. 1	2.1	0.3
Fort Collins No. 2	15.0	1.2
Loveland	10.8	1.1
Pueblo	5.2	0.1

[a]Based on dechlorination cost of $\$0.003/m^3$ water tested.

hazards to beneficial uses, and how cost estimates can be made and related to potential water quality benefits, is provided by Lee et al.[7,12] and Newbry.[10]

SUMMARY AND CONCLUSIONS

The practice of using chlorine for partial disinfection of WWTP effluents before discharge to the Colorado Front Range river systems studied results in effluents that contain sufficient chlorine to cause mortality of caged fish placed at the discharge within a few hours. The acutely toxic levels of chlorine are rapidly dissipated by dilution so that, in general, within a few hundred meters of the discharge, fish may reside in the river for periods of weeks to months without being significantly adversely affected.

Some reaches of each river investigated had chlorine concentrations exceeding chronic safe levels. Under worst-case conditions, the lengths of these reaches can be several kilometers. Implications of this to the water quality of the rivers studied are unclear at this time. However, numerous fish species are able to survive for long periods in these areas and procreate in or near them.

On the basis of these studies, extensive observations of the river systems, and review of previous work, we believe that removing chlorine from the WWTP effluents will not likely produce much, if any, improvement in the warmwater sports fisheries in the river reaches downstream from the discharges. This is because habitat and other characteristics of the river reaches are generally less than ideal for warmwater gamefish.

The hazard assessment approach developed in these studies should have general applicability to evaluating the hazards that chlorine and other contaminants arising from point-source discharges represent to the beneficial uses of aquatic systems. We recommend that this approach be used by those who manage aquatic systems for beneficial use protection.

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