# Residual Chlorine Impact Management Issues
# Comments on SWRCB Current Approach for Developing a Residual Chlorine Regulatory Program

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Over the past several years the California State Water Resources Control Board (SWRCB) staff have been developing a proposed regulatory approach for controlling the water quality impacts of residual chlorine used for water disinfection that is discharged to the State's waters. Recently the SWRCB has requested comments on its June 2006 proposed revised draft (SWRCB 2006) "Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California" (Residual Chlorine Policy). I wish to submit the following comments on this proposed policy. These comments are based on my having been involved in work on the aquatic chemistry of chlorine used for disinfection since the mid 1950s. This experience includes extensive field studies on the fate/persistence and toxicity of residual chlorine discharged by POTWs. A summary of this experience is presented below.

In the fall of 2005, when the SWRCB staff first announced its work on developing a regulatory policy for controlling water quality–toxicity impacts of residual chlorine discharged to the environment, I contacted Dena McCann (the SWRCB staff member responsible for the proposed Residual Chlorine Policy development) and brought to her attention my previous experience pertinent to the development a technically valid, cost-effective program to control adverse impacts of residual chlorine in discharges to the State's waters. I provided the SWRCB staff with hardcopies of several papers that I have published on this issue. These papers presented the results of the most comprehensive studies ever undertaken on the ambient water persistence and impacts of chlorine used for domestic wastewater disinfection.

In January 2006 I submitted comments to the SWRCB on the 2005 draft "Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California" (SWRCB 2005). These comments (Lee 2006) discussed several technical problems with the SWRCB staff's proposed Residual Chlorine Policy. These comments were not listed in the SWRCB's June 2006 "List of Comments" prepared by the SWRCB staff as presented on the SWRCB website. A copy of my January 2006 comments are available on my website at
http://www.members.aol.com/annejlee/ChlorinePolicyCom.pdf.

## Background to Comments

My work on chlorine began in 1955 where, at the University of North Carolina, Chapel Hill, my Master of Science in Public Health thesis was devoted to a study of the reactions of chlorine dioxide as they relate to the use of this chemical for treating domestic water supplies for taste and odor control. During these studies I used the amperometric titrator (discussed below) to measure the chlorine dioxide and other chlorine chemicals involved in this study.

My 1960 Harvard University PhD degree in Environmental Engineering/aquatic chemistry dissertation was devoted to the reactions of chlorine with phenol as they relate to production of chlorophenolic tastes and odors in domestic water supplies. This was one of the first studies that showed that chlorine reacts with some organics to produce what are now known as THMs (trihalomethanes).

During my 30-year university graduate-level teaching and research career, I conducted several studies devoted to chlorine chemistry as it applies to its use in domestic water supplies, swimming pools, domestic wastewaters and ambient waters. While teaching and conducting research in the graduate degree program in Environmental Engineering at Colorado State University during 1978-82, I conducted about $100,000 of studies on the fate/persistence and aquatic life toxicity of chlorine discharged by several Colorado Front Range domestic wastewater treatment plants to several Front Range streams/rivers. The chlorine was used at these treatment plants to disinfect the wastewater effluent to meet fecal coliform discharge limits. Comprehensive field studies were conducted of the persistence of chlorine discharged at four different wastewater treatment plants: Fort Collins (two plants) to the Cache La Poudre River, Colorado Springs to Fountain Creek, and Pueblo to Arkansas River. Each study took place over several days, where the concentrations of total residual chlorine where determine about every four hours to define the persistence of chlorine in the receiving waters for the wastewater discharge. At several locations studies were conducted during the summer and again in the winter. The chlorine concentrations were determined by amperometric titration with the titrator being powered by a portable electrical generator located on the river bank. This approach enabled reliable chlorine concentration determinations to be made down to about 5 ng/L within a few minutes of sample collection from the stream or river. The chlorine discharge plume that occurred in the river was defined on several occasions during the study period.

In addition, several measurements were made during the course of these studies to determine the characteristics of the parameters that influence the fate of chlorine discharged to the river/stream. These measurements included an assessment of sunlight-caused photo-decay of chlorine, chlorine demand of the river water, receiving water velocity, and mixing of the wastewater with the river/stream. This information was used to develop a differential-equation model of the fate/persistence of chlorine in the river/stream that can be used to predict the area of a river that could have concentrations of chlorine that would be toxic to aquatic life based on exceedance of the US EPA water quality criteria. These studies showed that residual chlorine can persist at potentially toxic levels for considerable distances (several thousand meters) in a river, especially under winter conditions of low temperature, low light, and low river flow.

Caged fish (fathead minnow adults) were located (anchored) at various locations within and outside of the wastewater treatment plant chlorine discharge plume. The cages were developed by Newbry and Lee (1984) from 4-in-diameter plastic pipe with plastic caps with many one-quarter-inch holes that allowed fairly free river-water passage through the cage. Every few hours during the several-day study period, each cage was examined to determine the number of live/dead fish. At the same time a sample of the river/stream water near the cage was obtained for chlorine analysis, which was performed at the edge of the stream. This approach enabled the development of chlorine concentration fish death relationships associated with the chlorine discharge plume.

It was found that integrated area average chlorine concentrations found near the cages matched the LC50 for fathead minnow adults, thereby confirming the laboratory-based US EPA chlorine water quality criteria. This approach for averaging chlorine concentrations is more reliable than the SWRCB's currently proposed arithmetic mean method (SWRCB 2006) for averaging chlorine concentrations as they may affect aquatic life toxicity.

A series of papers were developed from these studies, including

> Lee, et al. (1982), "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,"
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> Heinemann, et al. (1983), "Summary of Studies on Modeling Persistence of Domestic Wastewater Chlorine in Colorado Front Range Rivers,"
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> Newbry, et al. (1983), "Studies on the Water Quality Hazard of Chlorine in Domestic Wastewater Treatment Plant Effluents," and
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> Lee, G. F. and Jones, R. A. (1986), "Domestic Wastewater Dechlorination."

**Comments on the Presentations made at the SWRCB June, 2006, Hearing and on the Draft Revised Residual Chlorine Policy**

***Assessment of Impacts of POTW Residual Chlorine in Ambient Waters.*** Individuals representing domestic wastewater dischargers claimed at SWRCB meeting that there was no evidence that current discharge practices resulted in adverse impacts to fish populations. Such claims have little reliability, since in-depth, comprehensive studies were not conducted of the fish populations in the vicinity of the wastewater discharge where chlorine concentrations above about 10 µg per liter were consistently present in the receiving waters. Just because a casual observation fails to show dead fish in the vicinity of the discharge does not mean that chlorine discharges are not having an adverse impact on fisheries-related beneficial uses. There could readily be adverse impacts that are not discernable by casual observation. The above-discussed studies by Lee and his graduate students demonstrated that the residual chlorine discharged by POTWs is toxic to aquatic life. Detailed studies of the fish and other aquatic life populations in the area relative to habitat characteristics need to be conducted in order to discern the adverse effects of the residual chlorine. Lee and Jones (1982) have discussed an approach to determine if a particular wastewater discharge to a stream/river is having significant adverse impacts on the aquatic life in the area of the discharge.

***Fish Behavior near Chlorine Discharge Plumes.*** Observations made by Dr. Lee during the studies of the discharges to the Colorado Front Range streams/rivers in the vicinity of the residual chlorine discharge plume at and downstream of the discharge point showed that fish can experience short exposures to potentially toxic concentrations of chlorine without apparent significant adverse impacts. Fathead minnows that are naturally present in the Cache La Poudre River were observed foraging into the chlorine discharge plume. However, if the fish were placed in cages within the discharge plume, they were killed if the concentration duration of exposure exceeded the critical period. Fish placed in cages outside of the discharge plume survived during the test period, and, in one situation, survived for over a year. Downstream of the wastewater discharge point, if the discharge plume crosses the river/stream to the opposite side from the discharge point with a concentration above the US EPA water quality criterion, fish will not be able to readily gain access to low-chlorine waters and therefore could be damaged by the discharge.

***Low-Level Measurements of Residual Chlorine.*** Statements were made at the SWRCB June 2006 hearing that some equipment manufacturers claim that their equipment can continuously monitor chlorine at 1 ng/L. Such statements are highly questionable. As discussed above, I have been involved in low-level chlorine measurements since the mid-1950s. I developed an amperometric titration procedure that can reliably measure chlorine at a few ng/L. Rather than using a "dead-stop" approach, the titrator readings are plotted prior to and after the endpoint. This procedure has been included in Standard Methods for the Examination of Water and Wastewater (APHA, et al., 1995) Method 4500-Cl E Low-Level Amperometric Titration Method. As discussed above, this approach is readily adapted to field conditions with a small portable electric generator.

***Intermittent Chlorine Discharges.*** The SWRCB (2005) draft Residual Chlorine Policy included a section on regulating intermittent discharges of chlorine. This material was not included in the June 2006 revised draft. In the 1970s I conducted a study of the persistence of chlorine used to control electric generating station condenser fouling at the Philadelphia Electric Company Eddystone Electric Generating Station located on the Delaware Estuary (Lee 1979). The slugs of chlorine used to control condenser fouling were found to persist for considerable distances and time in the Estuary. The chlorine persistence was of sufficient magnitude to be adverse to aquatic life present in the discharge plume associated with the slugs of chlorine. There is need for the SWRCB to develop a regulatory approach for intermittent discharges of chlorine such as those that occur at electric generating stations practicing once-through waste heat dissipation with chlorine added to control heat exchange condenser fouling.

***Pipeline Disinfection Issues.*** Page 5 of the SWRCB's proposed revised Residual Chlorine Policy (SWRCB 2006) does not adequately address the potential impacts of chlorine used for pipeline disinfection. The "best management practices" approach is too nebulous. Guidance needs to be developed on requirements for controlling the potential water quality impacts of the excess chlorine discharged to the environment associated with pipeline disinfection. Contrary to the statement made in the revised draft June 2006 policy, it is possible to readily monitor the concentrations of residual chlorine in this type of discharge through the use of amperometric titration and a portable electric generator.

***Need for Continuous Monitoring.*** In the studies conducted on the fate/persistence and impacts of chlorine discharged by POTWs to Colorado Front Range streams/rivers, it was found that the concentrations of chlorine in the effluent from several POTWs were highly variable over time. Basically, the pattern seemed to exist that, with each operator shift change, the new operator would measure the chlorine and then adjust the dose. This was the dose of chlorine used for the next eight-hour shift. Little consideration was given to the fact that, during eight hours, the POTW effluent flow can change significantly, as can the concentration of chlorine demand in the effluent. Ideally, continuous measurement of chlorine should be practiced to eliminate this type of situation; however, reliable operation of continuous monitoring of residual chlorine at a few ng/L is, at best, difficult. If the operators will adjust the chlorine dose periodically, such as once per hour or so, to match flow and demand situations, it should be possible to accomplish adequate monitoring by making periodic measurements of residual chlorine. Allowing a POTW to follow this approach would require close supervision by the Regional Water Quality Control Boards, which may not be possible based on the Regional Boards' workloads.

The last paragraph on page 8 (SWRCB 2006) states,

> *"If grab samples taken at the end-of-pipe show chlorine residual above the stated effluent limit, the discharger must begin monitoring receiving water to adequately characterize and assess impacts to aquatic life within the receiving water. During situations where sampling the receiving water becomes a safety hazard, such as during the night in a swift moving river, the discharger can develop an alternative method to assess impacts to the receiving water and aquatic life. The Regional Water Board must approve the alternative method, however, prior to the exceedance."*

As summarized above, as an individual responsible for some of the most comprehensive studies ever conducted on the fate/persistence and impacts of POTW residual chlorine on receiving water quality, I am familiar with issues that need to be addressed in implementing the above-quoted statement. The first phase of any field study of a violation of an effluent limit for residual chlorine should be an assessment of the potential fate/persistence of residual chlorine in the receiving waters for a particular discharge. The modeling approach that we developed from our studies of Colorado Front Range streams/rivers lends itself to a few readily accomplished measurements of the receiving water characteristics to predict whether the concentrations of residual chlorine found in a particular effluent will exceed US EPA water quality criteria in the receiving waters for the discharge. With respect to assessing the "*… impacts to aquatic life within the receiving water,*" the caged fish assessment approach that we developed and conducted in Colorado is an approach that can help determine if the residual chlorine is causing aquatic life toxicity. While our papers summarizing this work have been published in peer-reviewed conference proceedings, they are not available electronically. I can, however, send hardcopies of them to anyone interested, upon request.

***Overall Assessment.*** It is my experience that there has been inadequate regulation of the potential impacts on receiving water quality of residual chlorine discharged by POTWs. These potential impacts have been well known for over 20 years. I have repeatedly observed that Regional Boards have allowed POTWs to periodically monitor the residual chlorine in their effluent using analytical methods that are inadequate to detect potential aquatic life toxicity that can occur below the allowed analytical method detection limits.

There has been and continues to be an urgent need for the SWRCB to adopt a uniform, protective approach for regulating the potential water quality impacts of residual chlorine discharged by POTWs and other sources. The June 2006 SWRCB proposed revised Residual Chlorine Policy is considerably improved over the December 2005 draft policy. However, as discussed herein, there are several areas that still need attention. They do not necessarily have to be incorporated into the final policy, but there is need to develop guidance covering implementation of the policy so that it will be uniform and protective of the State's waters.

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