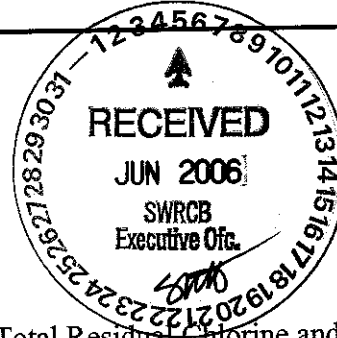


SCAP

Ms. Son Her, Clerk to the Board
State Water Resources Control Board
Executive Office
1001 I Street, 24th Floor
Sacramento, California 95814
Via e-mail: commentletters@waterboards.ca.gov



June 5, 2006

Subject: Comments on the April 2006 "Draft Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California"

Dear Ms. Her:

Tri-TAC (a technical advisory group that represents over 95% of the sewered population in the State through our sponsoring associations, the League of California Cities, the California Association of Sanitation Agencies and the California Water Environment Association), the California Association of Sanitation Agencies (CASA), the Bay Area Clean Water Agencies (BACWA), the Southern California Alliance of POTWs (SCAP), and the Central Valley Clean Water Agencies (CVCWA) would like to thank the State Water Resources Control Board members and staff for the process that has been used during this challenging effort to develop a statewide Policy for chlorine residual. We appreciate this opportunity to comment on the April 2006 "Draft Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California" (April 2006 Draft Policy). This significant regulatory initiative continues to be of high interest to POTWs throughout the State, who use chlorine and its derivatives to disinfect our effluent in order to meet our public health and water quality mandates.

Tri-TAC, CASA, BACWA, SCAP, and CVCWA represent wastewater agencies throughout California who collectively treat over 2 billion gallons of wastewater each day and serve over 95% of the sewered population in the State.

Our members have followed this proposed policy since it was first released in preliminary draft form. We have had many discussions with State Water Board staff regarding this proposed policy, always looking for the path to ensure that the State can meet its obligation to regulate the local clean water agencies with the goal of protecting California's water resources. We have provided to State Water Board staff the expertise of the laboratory and water quality experts at our respective agencies, these too are professionals who are dedicated to protecting California's water resources.

We have also contracted with EMA, a firm that specializes in control system technologies, to give us expert analysis regarding the potential of monitoring devices to meet the criteria set forth in the April 2005 Draft Policy. A copy of the report provided by EMA is attached to this letter.

We support the overall goal of the policy to limit the discharge of residual chlorine and chlorine-produced oxidants to receiving waters. We do not object to the use of EPA criteria for establishing water quality objectives for chlorine residual. Nevertheless we have significant concerns as described below.

We have reviewed the April 2006 Draft Policy and find there are a number of areas remaining where, consistent with our earlier comments, we believe compliance is simply not feasible. While some in the POTW community continue to question the need for this policy given the many regulatory and water quality challenges ahead of us, there does not appear to be any agency that can support the adoption of a policy that contains these overly prescriptive provisions that are not possible to comply with given currently available technology. We are concerned that if the April 2006 Draft Policy is adopted in its current form, wastewater treatment agencies throughout California will be in continuous jeopardy for non-compliance and associated mandatory fines and exposure to third party litigation.

A discussion of our specific areas of concern follows below.

1. Monitoring Requirements.

With respect to the specific monitoring requirements, it is our position they are not achievable. This position is based on actual experience with continuous monitoring systems as well as on information provided to us by EMA. EMA conducted an evaluation of the April 2006 Draft Policy with respect to the continuous monitoring requirement. A copy of the EMA report is attached to this letter. Based on information provided in the report as well as direct experience as reported by member agencies, specific aspects of the specifications for which we believe compliance is not possible have been identified. There aspects are:

- a. The required limit of detection is not achievable. The level of detection specified in the April 2006 Draft Policy is 1µg/L. According to the EMA report, for a wastewater matrix, "practical limits of the lowest concentrations that can be accurately measured are approximately 50 to 200 µg/L" – and that is in a laboratory versus actual field environment. These detection limits are on the order of 50 to 200 times that specified in the April 2006 Draft Policy.

In addition, while we understand several wastewater treatment agencies in California currently use continuous monitoring devices to measure total residual chlorine, the detection limits realized in the field are far above those mandated in the draft policy.

- b. The required accuracy is not achievable. The level of accuracy for continuous monitoring analyzers required to meet the criteria set forth in the April 2006 Draft Policy is 1µg/L. With respect to the objectives provided in the April 2006 Draft Policy (e.g., 11 µg/L, 13 µg/L, and 19µg/L), this level of accuracy is necessary in order to distinguish readings of 10 µg/L from 11 µg/L, 12 µg/L from 13 µg/L, 18 µg/L from 19 µg/L, and so forth. As indicated in the EMA report, "most chlorine analyzers have standard ranges of 0-2 or 0-5 mg/L, the accuracy is +/- 40 µg/L to 250 µg/L."

At this level of accuracy, a reading of 11 µg/L (the freshwater objective for a 4-day average) could reflect an actual concentration as low as zero and as high as 250 µg/L. It is simply not possible to obtain reliable readings using a continuous monitoring total residual chlorine analyzer within the range specified on the April 2006 Draft Policy.

- c. The required recording frequency is not achievable. The recording frequency specified in the April 2006 Draft Policy is “no less than one per minute.” While data recorders have the ability to record at this frequency, continuous monitoring total residual chlorine analyzers do not have the ability to respond at this frequency. According to the EMA report, “Response times of commercially available chlorine analyzers vary from 1.5 to over 10 minutes depending on the sample and reagent flow rates, internal volumes in the instrument, and whether the measurement is continuous or batch.” The frequency specified in the April 2006 Draft Policy is on the order of 1.5 to 10 times below that which is practically achievable.
- d. The QRL language is vague and ambiguous. It does not include any information on the accepted methodology for the determination of the QRL, how the feasibility of the QRL is assessed, or what method should be used by the Regional Water Boards to establish alternative QRLs. We would like to see a clearer process to establish QRLs and would welcome the opportunity to work with State Water Board staff in developing that process, including defining the elements of QRL studies that may be submitted by dischargers.
- e. Standard Method 4500-Cl E is not approved for wastewater testing. The Draft Policy specifies that the “discharger shall limit the calibration solution to no more than 0.500 ppm and verify the solution concentration by Method 4500-Cl E (Standard Methods).” Standard Method 4500-Cl E is not listed as an approved test method for the determination of total residual chlorine by USEPA in 40 CFR 136. We request clarification as to whether Method 4500-Cl E was correctly referenced in the Draft Policy and, if so, if any approved methods (as per 40CFR136) are also acceptable to the State Water Board for use under this Draft Policy. In addition, we request information regarding the process that was used by the State Water Board to validate the use of this method under the conditions specified.

2. Widespread Non-Compliance

Information provided by State Water Board staff indicates widespread non-compliance has not been reported in states where the EPA 1984 chlorine criterion has been adopted. To the best of our knowledge, no states have adopted a policy that combines the EPA criterion with the prescriptive continuous monitoring requirement set forth in the April 2006 Draft Policy. The Los Angeles County Sanitation Districts (LACSD) commissioned an informal survey to determine which states have adopted the USEPA 1984 chlorine criterion and, of those that had, what method of compliance was required (*Ref: 12/13/05 Larry Walker Associates Memorandum to LACSD entitled “Los Angeles County Sanitation Districts Total Residual Chlorine Survey Results”*).

The results of that study indicate none of the other states surveyed that have adopted the EPA 1984 criterion have the prescriptive monitoring requirements set forth in the April 2006 Draft Policy. In those instances where permit limits have been adopted that are below what can be measured, some states have made an allowance for technological limitations and consider all non-detected results to be below the MDL or zero.

To assume that there will not be widespread non-compliance with the April 2006 Draft Policy simply because widespread non-compliance has not been reported in other states is an unfounded and unreasonable position for the State Water Board to take. Since other states have not incorporated the prescriptive monitoring requirements specified in the April 2006 Draft Policy, it is not possible to conclude they will have no effect on the ability of the regulated community to comply.

In addition, the April 2006 "Economic Considerations For Proposed Total Residual Chlorine and Chlorine-Produced Oxidants Policy for California" indicates that data from prior discharge monitoring reports was used to assess what controls would be necessary to comply with the April 2006 Draft Policy. All non-detected values for chlorine which were reported as zero in prior discharge monitoring reports were also assumed to be non-detected under the April 2006 Draft Policy. Due to the differences in detection limits (the April 2006 Draft Policy requires significant lower sensitivity), this assumption is fundamentally flawed and results in a grossly incorrect financial estimate of impacts to agencies. In its current form, this policy would require a triple redundant analytical and control system at a cost of tens of thousands of dollars to meet a good faith effort. More importantly, it would require significant operating costs to staff a qualified instrument technician at every POTW throughout the state to keep this complex system calibrated and operational. All this cost would be incurred and it would still not be technically feasible to comply with the requirements of the proposed policy.

The assertion in the April 2006 "Economic Considerations For Proposed Total Residual Chlorine and Chlorine-Produced Oxidants Policy for California" that there would not be an impact in costs for agencies in complying with this policy as compared to their current system is completely inaccurate and furthers the flawed assumptions and conclusions in this critical document.

3. No Tolerance Approach

The April 2006 Draft Policy requires 100% compliance with the stated objectives. Many of the treatment system across the state are biological and require constant monitoring and operation to ensure that the system is working as intended. Supporting this process are many mechanical and technological devices, some of which have limitations. There is no acknowledgment of the technological limitations of operating an uninterrupted wastewater disinfection process. Short term duration spikes will and do occur. These spikes are not preventable and are not indicative of system failure. Rather, these spikes represent the balancing act between on-going system changes in chlorine demand and the accordant dechlorination agent demand. Wastewater treatment systems are designed to detect and respond to these changes. The best response times of these systems exceeds that allowed in the April 2006 Draft Policy such that routine spikes will occur that are of short-term duration. Operators (people) monitor and ensure that any spikes are

quickly resolved. For this reason, the Santa Ana Regional Board uses a criterion that is based on 99% compliance.

Because the proposed policy requires 100% compliance, the proposed policy would, in effect, establish an absolute technology-based standard without providing any margin for error. Because technology is inherently fallible, a policy such as this must include provisions to protect against violations based on limitations inherent in the underlying technology. (See, e.g., *FMC Corp. v. Train*, 539 F.2d 973 (1976)) and the 9th Circuit (*Marathon Oil v. EPA*, 564 F.2d 1253 (1977)). In its current form, the April 2006 Draft Policy does not include any such provisions.

The Water Code requires the State Water Board regulate to "attain the highest water quality which is reasonable" (Water Code section 13000). While it may be protective of water quality, we believe the April 2006 Draft Policy is not reasonable in that it does not protect against violations due to technological limitations.

4. Method of Compliance

The April 2006 Draft Policy specifies the means by which compliance with the total residual chlorine objectives must be met. While we support the establishment of a numeric objective for total residual chlorine, we believe the means by which compliance is achieved should be determined by the permittee. This is supported by Section 13360(a) of the Water Code which states:

"No waste discharge requirement or other order of a regional board or the state board or decree of a court issued under this division shall specify the design, location, type of construction, or particular manner in which compliance may be had with that requirement, order, or decree, and the person so ordered shall be permitted to comply with the order in any lawful manner."

In order to provide a means of compliance that is implementable and achievable, we request that other means of compliance, such as measuring dechlorinating agent residual with a continuous monitoring analyzer or by otherwise demonstrating the presence of dechlorinating agent in the plant effluent (stoichiometric). We offer the following suggested clarification language:

"Compliance can be demonstrated using any of the following three methods:

- a. Show an absence of residual chlorine in the plant effluent through continuous measurement of chlorine residual using a continuous monitoring analyzer;*
- b. Show an absence of residual chlorine by showing a presence of dechlorinating agent in the plant effluent through continuous measurement of dechlorinating agent residual using a continuous monitoring analyzer;*
- c. Show an absence of residual chlorine by showing a presence of dechlorinating agent in the plant effluent through continuous measurement of chlorinated effluent chlorine residual, dechlorinating agent feed rate, and plant flow (or other combination of plant parameters that*

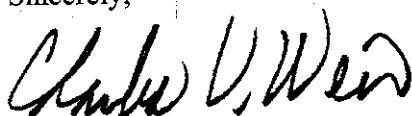
demonstrate compliance stoichiometrically). When using sulfur dioxide (SO₂) as the dechlorinating agent the stoichiometric relationship requires on the order of 1.0 part sulfur dioxide to remove 1.0 part of chlorine residual. Compliance determinations shall be based on the demonstration that every pound of chlorine measured immediately prior to dechlorination is treated with greater than 0.9 pound of sulfur dioxide. When using sodium bisulfite (NaHSO₃) as the dechlorinating agent the stoichiometric relationship requires on the order of 1.61 parts sodium bisulfite to remove 1.0 part of chlorine residual. Compliance determinations shall be based on the demonstration that every pound of chlorine measured immediately prior to dechlorination is treated with greater than 1.61 pounds of sodium bisulfite."

In addition, to provide a vehicle for the development and implementation of new monitoring methods, we request the policy be revised to allow the discharger to submit data on proposed alternative continuous monitoring methods to their local regional board and to grant regional boards the authority to review and approve such methods for use in lieu of the methods identified above.

After reviewing the April 2006 Draft Policy, we are concerned that a number of the significant items previously raised by Tri-TAC in comment letters and during public workshops have not been addressed in any manner. These items remain of significant concern and directly relate to our ability to comply with the April 2006 Draft Policy. We sincerely hope our concerns will be addressed so that we can work with the State Water Board and our Regional Water Board to attain reasonable compliance with this important policy.

We appreciate the opportunity to provide comments to State Water Board staff during this comment period. We would be pleased to meet with you to discuss further revisions to the draft policy prior to formal release. If you have any questions regarding the comments presented in this letter, please do not hesitate to contact the Tri-TAC Water Committee Co-Chair, Ben Horenstein, at (510) 287-1846.

Sincerely,



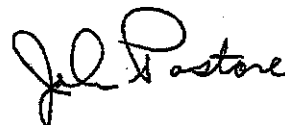
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June 5, 2006

Ms. Marlaigne Dumaine
California Association of Sanitation Agencies
925 L Street, Suite 1400
Sacramento, California 95814

Dear Ms. Dumaine,

EMA has thoroughly reviewed and prepared comments on the State Water Resources Control Board (SWRCB) draft Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California dated April 2006 to assist the California Association of Sanitation Agencies and its Tri-TAC partners in evaluating the impact of implementing these future regulations. Complete detailed comments are attached. The key comments are:

- The analytical method required by the policy for measurement of (total) chlorine residual in wastewater effluents, Method 4500-Cl E, is not listed as an acceptable method for wastewaters (Standard Methods pp. 4-54 through 4-55).
- Even if Method 4500-Cl E was acceptable for wastewater effluents, the 4-day limit of 11 ug/L is only 1 ug/L above the detection limit of the procedure under the best of laboratory conditions. It is unrealistic to think that on-line analyzers could reliably perform anywhere close to this level of detection. Even though several chlorine analyzers state that their accuracy is between 1 and 5 ug/L Cl₂, these claims should be regarded as highly suspect since the detection limit of the best accepted analytical method is 10 ug/L. An accuracy of +/- 40 ug/L to 250 ug/L is realistically the best achievable with commercially available on-line analyzers.
- Response times of commercially available chlorine analyzers varies from 1.5 to over 10 minutes. Although chlorine analyzers provide an output signal that can be sampled every minute, this signal is really a time weighted average over a period (or a batch); not an independent analysis every minute as required by the policy.

- Even if there were chlorine analyzers that could perform reliably with a 1 ug/L accuracy, it would be near impossible to control the residual chlorine level between 0 and 11 ug/L because of the inherent dead times and response times associated with the process, the sampling systems, the analyzers themselves, and the chemical feed systems. In general, disturbances in chlorine concentration and flow rates can occur faster than the analyzers can measure and the control system correct even when all equipment is working correctly.

Based upon these observations, EMA has several recommendations for the State Water Resources Control Board regarding implementation of the Total Residual Chlorine and Chlorine-Produced Oxidants Policy of California.

1. Since the primary requirement of measuring residual chlorine in the range of 0 to 11 ug/L is not achievable, mandatory penalties for non-compliance should be removed. Measurement of dechlorination reagent and stoichiometry should be the two primary methods of determining compliance rather than backup methods.
2. The section describing the detection limits and calibration requirements must be cleaned up for technical correctness or should be removed altogether.
3. The requirement for 100% compliance is unrealistic and should be modified. Even the space shuttle with it's triple redundancy has not been 100% reliable.
4. The State Water Resources Control Board should sponsor a comprehensive test of dechlorination analyzers through a neutral third party (such as the Instrumentation Testing Association) to demonstrate performance and maintenance requirements under field conditions before requiring such instruments be used at every wastewater treatment plant in the state.

We appreciate this opportunity to work with you on this topic of so much importance to the state of California and the nation as a whole. If you have any questions, please feel free to call me at 281-300-8367. If desired, I would be glad to provide direct testimony to the State Water Resources Control Board on behalf of the California Association of Sanitation Agencies and its Tri-TAC partners.

Sincerely,



Dr. Bob Hill, P.E.
Principal Consultant
EMA, Inc.

DRAFT TRC & CPO POLICY OF CALIFORNIA

SCOPE OF REVIEW

EMA reviewed the State Water Resources Control Board (SWRCB) draft Total Residual and Chlorine-Produced Oxidants Policy of California dated April 2006 (the POLICY). Our primary purpose was to comment on the practicality of the proposed effluent chlorine limits from an instrumentation and control perspective. EMA, Inc. is well qualified to provide such a review and has over 30 years of leadership in automation of water and wastewater facilities. Dr. Bob Hill of EMA, the primary author of this document, has 25 years of automation experience including over 12 years of hands-on operations and maintenance experience with chlorination and dechlorination systems at 35 wastewater treatment plants.

Method of Residual Chlorine Analysis

The POLICY states that all off-line measurements of chlorine residual shall be performed using Method 4500-Cl E. These measurements include confirmation readings and calibration data associated with the chlorine analyzers and standardizing solutions as well as other uses. Method 4500-Cl E, however, is not listed as an acceptable method for wastewaters (Standard Methods, 20th Edition, pp. 4-54 through 4-55). Therefore, EMA questions why an unapproved method would be listed as the only acceptable methodology in the POLICY.

Even if Method 4500-Cl E was acceptable for wastewater effluents, the 4-day limit for fresh water discharges is 11 µg/L or only 1 µg/L above the detection limit of the procedure under the best of laboratory conditions. It is unrealistic to think that on-line analyzers could reliably perform anywhere close to this level of detection. The case for saltwater discharges is even worse in that the 4-day average limit is 7.5 µg/L or 2.5 µg/L BELOW the detection limit of the specified methodology.

Chlorine Analyzer Requirements

The POLICY has several requirements for on-line chlorine analyzer performance. It states that the "On-line chlorine residual devices must record measurements at no less than one per minute and record concentrations in parts per billion (µg/L or ppb)." While this is probably somewhat of a wording problem, it seems appropriate to point out that on-line analyzers typically do not record data at all. They output a signal (analog or digital) that is recorded by a SCADA or process control system. But if taken literally, no commercially available on-line chlorine analyzer will meet this requirement.

The POLICY also states that "On-line devices must have a manufacturer's stated detection limit, scale range, or sensitivity below the permitted effluent limit." This statement is very confusing as discussed below. The intention of the POLICY should be clarified using the correct terms. Adding definitions of these terms to the POLICY would be most useful.

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Detection Limit: By convention and from statistics, detection limit (DL) is defined as the concentration corresponding to a signal three times the noise level of the background. Detection limit is commonly understood to be the smallest concentration we can measure with a particular technique. In fact it is the point at which we can make a decision whether the compound is **present or not** but not necessarily make an accurate measurement.

For instrumental methods of analysis an **IDL** (Instrument Detection Limit) is the lowest limit that the instrument can detect. It is determined on samples which have not gone through any sample preparation steps. An **MDL** (Method Detection Limit) is similar to an **IDL**, but is based on samples which have gone through the entire sample preparation scheme prior to analysis. A **PQL** (Practical Quantification Limit) is normally 3 to 10 times the **MDL** and is considered the lowest concentration that can be accurately measured, as opposed to just detected. **DLs** are actually determined by analysis of replicate low-level samples or blanks. This information gives the variation in instrument response at levels near the detection limit, from which 99% confidence limits are calculated from the standard deviation.

From a practical point of view based on the definition of detection limit, accurate measurements can be made at residual chlorine concentrations as low as 30 to 100 µg/L in clean water under ideal laboratory conditions. Since the detection limit in a wastewater matrix is much higher, practical limits of the lowest concentrations that can be accurately measured are approximately 50 to 200 µg/L.

Scale and Range: The POLICY states that the "scale range" must be below the permitted effluent limit. This statement is confusing since "scale" and "range" are two separate terms. Scale is the actual display device (usually an electronic component). However, the term "full scale" is often used to mean range. Range is the difference between the highest and lowest measurements concentrations. For instance, an instrument that can measure between 0 and 0.5 mg/L has a range of 0.5 mg/L. Assuming that the correct term was range, the statement still makes no sense because it requires the range to be less than the permitted effluent limit (e.g., 0 to 10 µg/L). Later in the same paragraph, the POLICY states that the maximum calibration concentration should be 500 mg/L. This value should probably be 500 µg/L to be consistent with the intent. Clarification is required.

Sensitivity versus Accuracy: Inexplicably, the POLICY does not specify an accuracy (or error) for on-line residual chlorine analyzers. They do specify that the sensitivity must be less than the permitted effluent limit. This requirement, however, just means that the instrument can differentiate between 100 µg/L and 101 µg/L regardless of calibration or accuracy. We suggest that a reasonable accuracy specification be developed for the POLICY.

Commercially Available Chlorine Analyzers

Previous comments have documented that no currently available residual chlorine analyzers meet the requirements of the POLICY. The following is therefore a very abbreviated discussion.

Accuracy: Several chlorine analyzers state that their accuracy (really meaning error) is between 1 and 5 µg/L Cl₂. These claims should be regarded as highly suspect since the detection limit of the best accepted analytical method is 10 µg/L for clean samples under ideal laboratory conditions. Most analyzers have errors that are stated as +/-2% to 5% of full scale. Since most

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chlorine analyzers have standard ranges of 0-2 or 0-5 mg/L, the accuracy is +/- 40 µg/L to 250 µg/L. In published field test reports, the Instrumentation Testing Association used four consecutive conformation errors of 200 µg/L in the same direction as an indication that instrument calibration or maintenance was required. This standard seems to be a practical one for on-line chlorine analyzers.

One Minute Readings: Response times of commercially available chlorine analyzers vary from 1.5 to over 10 minutes depending on the sample and reagent flow rates, internal volumes in the instrument, and whether the measurement is continuous or batch. Although chlorine analyzers provide an output signal that can be sampled every minute, this signal is really either a time weighted average over a period or a discrete value for each batch analysis; but not an independent analysis every minute as required by the POLICY.

Sampling Systems

The POLICY is silent on a number of important topics that affect instrument readings. A major concern is the proper design of the sampling system. All of the amperometric-based and DPD colorimetric chlorine analyzers utilize pumped sample systems. This pumping sampling system affects the sample in several ways.

From a control aspect, the sampling system adds dead time which complicates how quickly disturbances can be measured and how fast the control system can compensate for those disturbances.

Since dechlorinated samples are, by definition, low in chlorine, biological growth will occur in the sample piping (or tubing). This growth has the affect of decreasing the chlorine residual. Therefore, the sample that the analyzer "sees" has a lower chlorine concentration than the bulk liquid. [This phenomenon suggests that perhaps the easiest way to meet the POLICY is to design a long detention time sampling system and never clean it.]

Chlorine usually resides as hypochlorous acid or hypochlorite ion in solution depending primarily on pH. However, these reactions are reversible and chlorine gas can be vaporized and lost as a gas if the sample is placed under a suction with vigorous agitation (per Standard Methods). One ramification from this phenomenon is that submersible sample pumps should be used so that the sample is always pressurized.

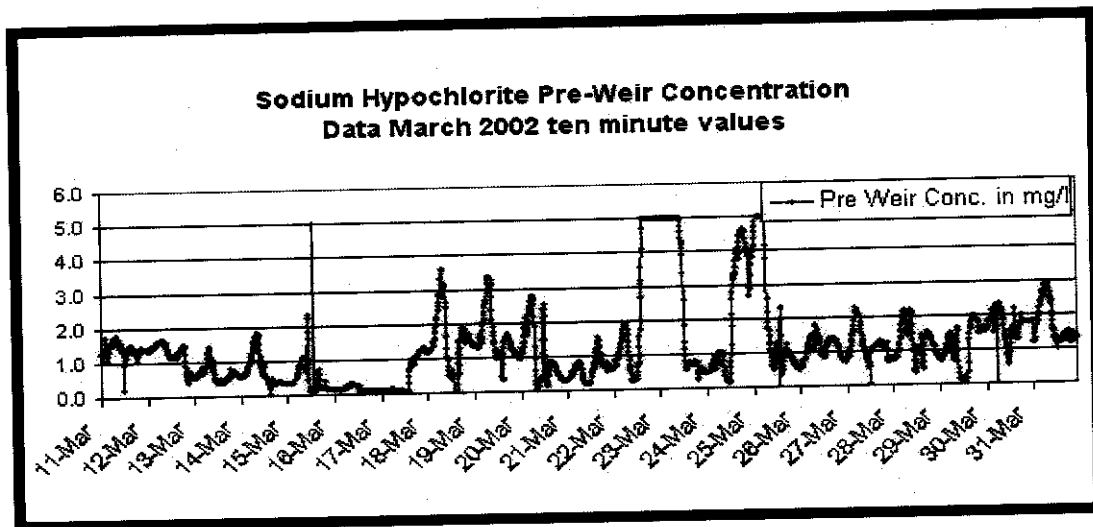
Interactions That Affect Control

Even if there were chlorine analyzers that could perform reliably with a +/- 1 µg/L accuracy and a fast response time, it would be impossible, in most instances, to control the residual chlorine level between 0 and 11 µg/L with no excursions because of process disturbances, the inherent dead times, response times, and errors associated with the process, the sampling systems, the analyzers themselves, and the chemical feed systems.

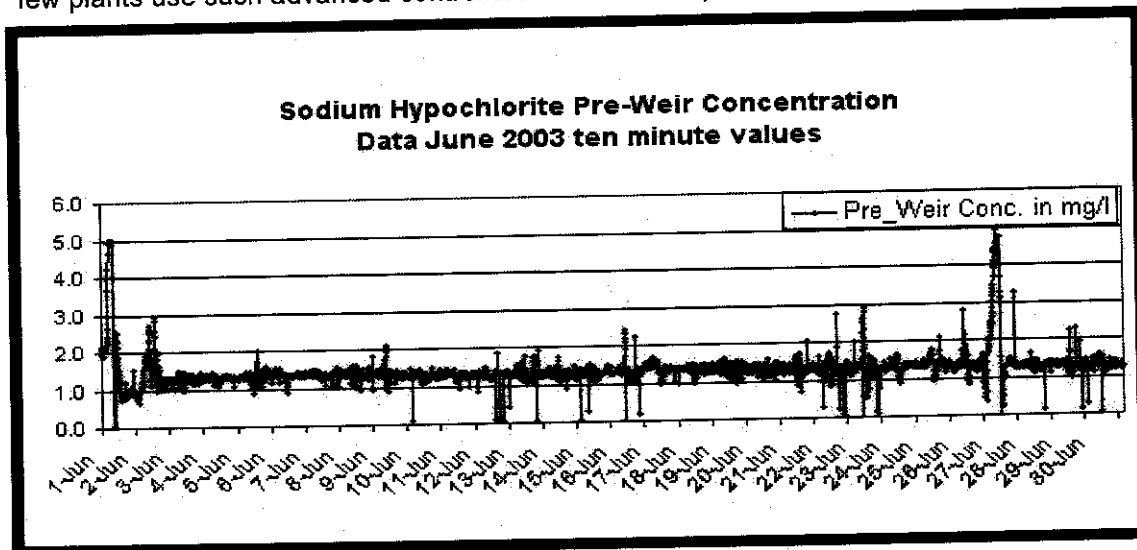
To give a few examples, chlorination itself is difficult to control. It is affected by chlorine demand (with a time constant of minutes to hours), flow rates (with a time constant of a few minutes), and a long and variable detention time that is a function of effluent flow rate. The time between the

point of chlorine addition and the final effluent measurement is commonly 90 to 180 minutes and is usually pure dead time.

The following figure shows residual chlorine concentrations at a non-California WWTP with manual control. There are significant minute-to-minute variations as well as some apparent instrument malfunctions. Controlling dechlorination with this type of input is very difficult but is the most common practice.



There are several advanced control strategies that can result in much better performance than is possible with manual control. One is internal model control (IMC) that utilizes a mathematical model to predict what the residual chlorine concentration will be based on the detention time and a rate of reaction. The following figure shows results at the same plant after implementing IMC. Obviously control has been tightened up considerably even though there are still periodic excursions. Dechlorination is much easier to control with an input such as this. Unfortunately few plants use such advanced controllers to achieve improved control.



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Another common source of dead time comes from chemical feed systems. A typical chlorine or sulfur dioxide (SO₂) feed system consists of dissolving the gas into a water stream through an eductor. This stream then flows through a pipe as a liquid to the point of application. Changes in feed rate are made by modulating the gas flow rate into the eductor and thereby changing the concentration in the liquid carrier. These changes, however, must travel as a plug through the pipe to the point of addition. The detention time for such systems are often 5 to 15 minutes and sometimes longer. So even if an analyzer measures a chlorine residual that is too high, it may take 5 or more minutes before the SO₂ chemical feed system can adjust to the new concentration.

In general, disturbances in chlorine concentration and flow rates can occur faster than the analyzers can measure and the control system correct even when all equipment is working correctly.

No Accounting For Short-Term Failures

The POLICY doesn't seem to take into account that all processes and control systems will periodically have at least some short-term emergency (non-planned maintenance) failures. These can occur from a wide variety of diverse events such as a sticky control valve, a valve incorrectly opened or closed, a clogged sample pump, a power failure (or restart), an operator error, a switchover between cylinders, or simply running out of chemical. These types of events are seemingly inevitable even in sophisticated systems such as the space shuttle that utilize triple redundancy for all major subsystems.

Feeding Excess Sulfite

Since residual chlorine concentrations cannot be measured and controlled in the range of interest listed in the POLICY, the only practical way that utilities can meet the chlorine permit limits will be to grossly overfeed their dechlorinating agent. Others have previously commented on the additional costs, decreased safety, and possible effluent toxicity aspects of this result. It will also promote the proliferation of sulfur reducing bacteria in an effluent that should be almost sterile.

Sulfite and Dechlorination Analyzers

The POLICY allows the direct measurement of the dechlorinating agent (usually dissolved sulfite) as a backup method to prove that some chlorine residual exceedances are false positives. Since no on-line chlorine analyzers can meet the requirements specified in the POLICY, it would be better to make this measurement the primary means of determining compliance.

There are two primary methods for determining the effluent sulfite concentration. One methodology adds a standard dose of chlorine to the dechlorinated effluent sample and then measures the chlorine concentration. For instance, if 2.0 mg/L chlorine is added and the

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measured residual chlorine concentration is 1.8, the calculated sulfite concentration is 0.2 mg/L (in chlorine equivalents).

A second type of instrument acidifies the effluent sample converting sulfites to SO_2 . The SO_2 is then stripped out of the liquid phase and measured as a gas by a sensor. One advantage of this instrument is that the sample never touches the sensor itself.

Unfortunately there are only a few such dechlorination instruments available on the market. There has been very little third party verification of the performance and maintenance requirements of these instruments under field conditions.

EMA recommends that the State Water Resources Control Board sponsor a comprehensive test of dechlorination analyzers through a neutral third party (such as the Instrumentation Testing Association) to demonstrate performance and maintenance requirements under field conditions before requiring such instruments be used at every wastewater treatment plant in the state.

References

Instrumentation Testing Association, "Performance Evaluation of Residual Chlorine Analyzers for Water and Wastewater Treatment Applications," Report CH-1, November 1990.

Instrumentation Testing Association, "Total and Free Chlorine Residual Analyzers: Maintenance Benchmarking Study," Report MBS99CL-001, 1999.

Instrumentation Testing Association, "Sacramento Regional Wastewater Treatment Plant Online Chlorination and Dechlorination Analyzers Performance Evaluation Report," Report PER04CI-006, 2004.